System Characterization, Modelling, Designing and Integrative Analysis of Nanosystems

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Under the supervision of

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DECLARATION

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material that is original in this work. It is being submitted for the Degree of Master of Engineering at the Thapar University, Patiala, Punjab, India. It has not been submitted before any degree or examination in any other University.

This is to certify that above declaration made by the student concerned is correct to the best of my knowledge and belief.

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ABSTRACT

Much of the fascination with nanotechnology stems from these quantum and surface phenomena that matter exhibits at the nanoscale. Two main approaches are used in nanotechnology. In the "bottom-up" approach, materials and devices are built from molecular components which assemble themselves chemically by principles of molecular recognition. In the "top-down" approach, nano-objects are constructed from larger entities without atomic-level control. Nanotechnology is considered a key technology for the future. Nanotechnology entails the application of fields of science as diverse as surface science, organic chemistry, molecular biology, semiconductor physics, micro-fabrication, etc. Nanotechnology distinct from devices which are merely miniaturized versions of an equivalent macroscopic device; such devices are on a larger scale and come under the description of micro technology In this thesis work, an attempt is made to develop an integrated systems model for the structure of the nanotechnology system in terms of its constituents and interactions between the constituents and processes etc, using graph theory and matrix algebra. The nanotechnology system is first modelled with the help of graph theory, then by a variable adjacency matrix and then by a multinomial known as a permanent function. The permanent function provides an opportunity to carry out structural analysis of the nanotechnology system in terms of strength, weakness, improvement and optimization by correlating the different system with its structure. A physical meaning has been associated with each term of the permanent function. Different structural attributes of the nanotechnology system are identified to develop a graph theoretic model, a matrix model and a multinomial permanent model of the nanotechnology system. A top-down approach for complete analysis of any nanotechnology system is also given. A general methodology is also presented for characterization and comparison of two nanotechnology systems. Usefulness of the present methodology is also illustrated. While modelling a nanotechnology system, nanomaterial selection is one of the mostly encountered decision problems in material science literature, is still an onerous task for manufacturing organisations. Problem has become more difficult in recent years due to increasing complexity, available features, and facilities offered by different nanomaterial products. Here generation and maintenance of reliable and exhaustive data of nanomaterial based on their different pertinent attributes is done. It is useful for better understanding, comparison and analysis and for comparison; ranking and optimum selection of nanomaterial from a large number of nanomaterial available in global market, the multiple attribute decision making problems is solved by “TOPSIS” (Technique for Order Preferences by Similarity to Ideal Solution). The techniques convert database into knowledge base by considering normalization, relative weights, positive benchmarked and negative benchmarked solutions and normalized weighted database into single numerical suitability index for each candidate nanomaterial solution. It helps the nanomaterial user to save time by providing a tool for selecting the nanomaterial most suited for his operational needs. The selection procedure allows rapid convergence from large number of candidate nanomaterial to a manageable shortlist of potentially suitable nanomaterial using elimination search based on the few critical selection attributes. Subsequently, the selection procedure proceeds to rank the alternatives in the shortlist by employing different attributes based specification and graphical methods. The ranks of the candidate nanomaterial are calculated with respect to the best possible nanomaterial, say +ve benchmark nanomaterial, for particular application. The coding scheme and the selection procedures, mathematical and graphical, are illustrated with example. After selecting appropriate nanomaterial as per the requirements for designing nanodevices organizations are deploying well designed nanoactuators supporting converged applications of defence, mechanical industry and biological applications etc. Use of different applications demands nanoactuator to have various abilities – actuation, modification,

realization, performance etc, called x- abilities- in varying degree of importance depending on application requirements of an organization. To facilitate design of nanoactuator simultaneously for all x – abilities in an integrated way, a concurrent design methodology using multiple attribute decision making (MADM) approach is proposed. This concurrent design methodology is aimed at including design time considerably and makes use of expertises of experts from different specialized fields in a single design team. MADM approach provides technique for selection of best nanoactuator for the application under consideration. In this way, with proper system characterization, analysis and designing of the nanosystems may lead to a better production of the nanodevices as per the required applications.

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16 **July**, 2012

Tanvir Singh

University Roll No:-801082028

DEDICATIONS

I sincerely dedicate this work to my lovable Parents.....

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INTRODUCTION

1. Nanotechnology System

1.1. Introduction to Nanotechnology System

Nanotechnology is a term that is used to describe the science and technology related to the control and manipulation of matter and devices on a scale less than 100 nm in dimension. It involves a multidisciplinary approach involving fields such as applied physics, materials science, chemistry, biology, surface science, robotics, engineering, electrical engineering and biomedical engineering. At this scale the properties of matter is dictated and there are few boundaries between scientific disciplines. Nanotechnology (sometimes shortened to "nanotech") is the study of manipulating matter on an atomic and molecular scale. Generally, nanotechnology deals with developing materials, devices, or other structures with at least one dimension sized from 1 to 100 nanometres. Quantum mechanical effects are important at this quantum-realm scale. Nanotechnology is considered a key technology for the future. Consequently, various governments have invested billions of dollars in its future. The USA has invested 3.7 billion dollars through its National Nanotechnology Initiative followed by Japan with 750 million and the European Union 1.2 billion. Nanotechnology is very diverse, ranging from extensions of conventional device physics to completely new approaches based upon molecular self-assembly, from developing new materials with dimensions on the nanoscale to direct control of matter on the atomic scale. Nanotechnology entails the application of fields of science as diverse as surface science, organic chemistry, molecular biology, semiconductor physics, micro fabrication, etc. Scientists debate the future implications of nanotechnology. Nanotechnology may be able to create many new materials and devices with a vast range of applications, such as in medicine, electronics, biomaterials and energy production. On the other hand, nanotechnology raises many of the same issues as any new technology, including concerns about the toxicity and environmental impact of nanomaterial **[1]** and their potential effects on global economics, as well as speculation about various doomsday scenarios. These concerns have led to a debate among advocacy groups and governments on whether special regulation of nanotechnology is warranted

1.2. Origin of Nanotechnology

Although nanotechnology has been around since the beginning of time, the discovery of nanotechnology has been attributed to Richard Feynman[1] who presented a paper called ‘There is Plenty of Room at the Bottom’ on 29 December 1959 at the annual meeting of the American Physical Society. Feynman talked about the storage of information on a very small scale, writing and reading in atoms, about miniaturization of the computer, building tiny machines, tiny factories and electronic circuits with atoms. He stated that ‘In the year 2000, when they look back at this age, they will wonder why it was not until the year 1960 that anybody began seriously to move in this direction’. However, he did not specifically use the term ‘nanotechnology’. _The first use of the term ‘nanotechnology’ has been attributed to Norio Taniguchi[2] in a paper published in 1974 “On the Basic Concept of ‘’Nanotechnology”. Since then several definitions[3] of nanotechnology have evolved. For example, the dictionary

definition states that nanotechnology is ‘the art of manipulating materials on an atomic or molecular scale especially to build microscopic devices’. Other definitions include the US government which state that ‘Nanotechnology is research and technology development at the atomic, molecular or macromolecular level in the level in the length scale of approximately 1-100 nm range, to provide a fundamental understanding of phenomena and materials at the nanoscale and to create and use structures, devices and systems that have novel properties and functions because of their small and/or intermediate size’. The Japanese have come up with a more focused and succinct definition for ‘True Nano’ as nanotechnology which is expected to cause scientific or technology quantum jumps, or to provide great industrial applications by using phenomena and characteristics peculiar in nano-level. Regardless of the definition that is used, it is evident that the properties of matter are controlled at a scale between 1 and 100 nm. Although nanotechnology is a relatively recent development in scientific research, the development of its central concepts happened over a longer period of time. The emergence of nanotechnology in the 1980s was caused by the convergence of experimental advances such as the invention of the scanning tunnelling microscope in 1981 and the discovery of fullerenes in 1985, with the elucidation and popularization of a conceptual framework for the goals of nanotechnology beginning with the 1986 publication of the book Engines of Creation.

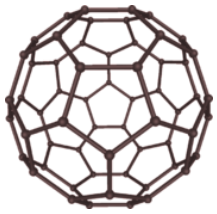


Figure-1.1.Buckminsterfullerene C_{60},

This is also known as the buck ball, is a representative member of the carbon structures known as fullerenes. Members of the fullerene family are a major subject of research falling under the nanotechnology umbrella.

The scanning tunnelling microscope, an instrument for imaging surfaces at the atomic level, was developed in 1981 by Gerd Binnig and Heinrich Rohrer at IBM Zurich Research Laboratory, for which they received the Nobel Prize in Physics in 1986 **[2]** Fullerenes were discovered in 1985 by Harry Kroto, Richard Smalley, and Robert Curl, who together won the 1996 Nobel Prize in Chemistry **[3. 4]** Around the same time, K. Eric Drexler developed and popularized the concept of nanotechnology and founded the field of molecular nanotechnology. In 1979, Drexler encountered Richard Feynman's 1959 talk "There's Plenty of Room at the Bottom". The term "nanotechnology", originally coined by Norio Taniguchi in 1974, was unknowingly appropriated by Drexler in his 1986 book Engines of Creation: The Coming Era of Nanotechnology, which proposed the idea of a nanoscale "assembler" which would be able to build a copy of itself and of other items of arbitrary complexity. He also first published the term "grey goo" to describe what might happen if a hypothetical self-replicating molecular nanotechnology went out of control. Drexler's vision of nanotechnology is often called "Molecular Nanotechnology" (MNT) or "molecular manufacturing," and Drexler at one point proposed the term "zettatech" which never became popular. In the early 2000s, the field was subject to growing public awareness and controversy, with prominent debates about both its potential implications, exemplified by the Royal Society's report on nanotechnology, **[5]** as well as the feasibility of the applications envisioned by advocates of

molecular nanotechnology, which culminated in the public debate between Eric Drexler and Richard Smalley in 2001 and 2003. **[6]** Governments moved to promote and fund research into nanotechnology with programs such as the National Nanotechnology Initiative. The early 2000s also saw the beginnings of commercial applications of nanotechnology, although these were limited to bulk applications of nanomaterial, such as the Silver Nano platform for using silver nanoparticles as an antibacterial agent, nanoparticle-based transparent sunscreens, and carbon nanotubes for stain-resistant textiles **[7].**

1.3. Approaches to Nanotechnology

Numerous approaches have been utilized successfully in nanotechnology, and as the technology develops further approaches may emerge. The approaches employed thus far have generally been dictated by the technology available and the background experience of the researchers involved. Nanotechnology is a truly multidisciplinary field[4] involving chemistry, physics, biology, engineering, electronics, social science, etc., which need to be integrated together in order to generate the next level of development.

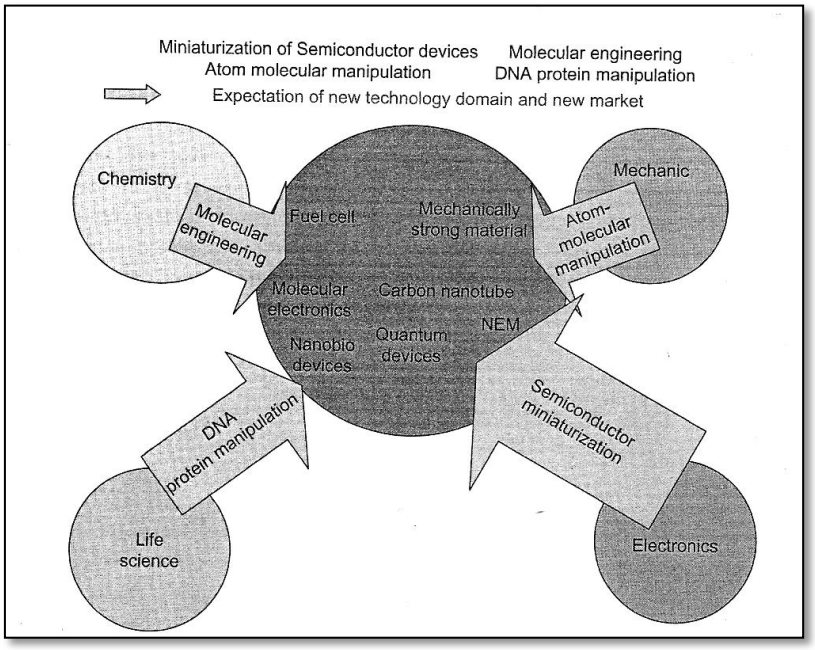


Figure 1.2.Multidisciplinary nature of nanotechnology

Fuel cells, mechanically stronger materials, nanobiological devices, molecular electronics, quantum devices, carbon nanotubes, etc. have been made using nanotechnology. Even social scientists are debating ethical use of nanotechnology.

The two main approaches to explaining nanotechnology to the general public have been oversimplified and have become known as the 'top-down' approach and the 'bottom-up' approach.

1.3.1. Top-down approaches

These seek to create smaller devices by using larger ones to direct their assembly.

- Many technologies that 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 magneto resistance-based hard drives already on the market fit this description, as do atomic layer deposition (ALD) techniques. Peter Grünberg and Albert Fert received the Nobel Prize in Physics in 2007 for their discovery of Giant magneto resistance and contributions to the field of spintronics.
- Solid-state techniques can also be used to create devices known as nanoelectromechanical systems or NEMS, which are related to microelectromechanical systems or MEMS.
- Focused ion beams can directly remove material, or even deposit material when suitable pre-cursor gasses are applied at the same time. For example, this technique is used routinely to create sub-100 nm sections of material for analysis in Transmission electron microscopy.
- Atomic force microscope tips can be used as a nanoscale "write head" to deposit a resist, which is then followed by an etching process to remove material in a top-down method.

The top-down approach involves fabrication of device structures via monolithic processing on the nanoscale. This approach has been used with spectacular success in the semiconductor devices used in consumer electronics. The most successful industry utilizing the top-down approach is the electronics industry

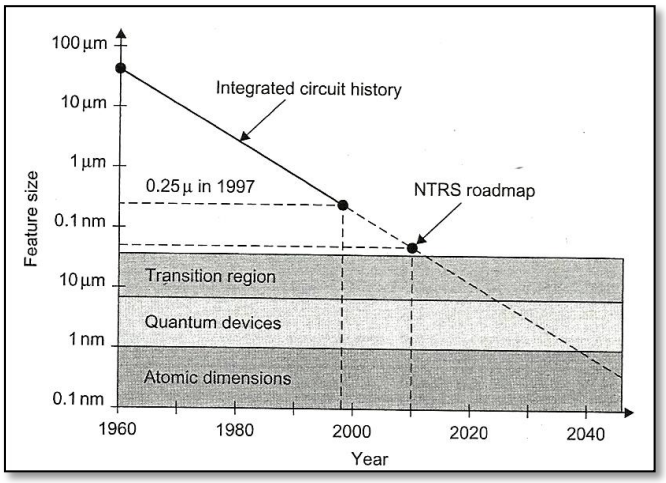


Figure-1.3. Features size evolution in silicon chips

This industry is utilizing techniques involving a range of technologies such as chemical vapour deposition (CVD). Physical vapour deposition (PVD), lithography (photolithography, electron beam and X-ray lithography), wet and plasma etching, etc. to generate functional structures at the micro- and nanoscale

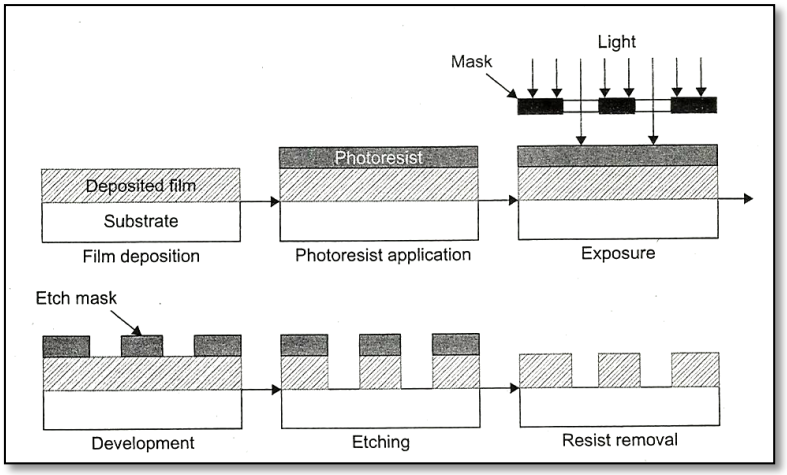


Figure-1.4. A typical process sequences employed in the electronics industry to generate functional devices at the micro and nanoscale.

Evolution and development of these technologies have allowed emergence of the numerous electronic products and devices that have enhanced the quality of life throughout the world. The feature sizes have been shrinking continuously from about 75µm to below 100 nm. This has been achieved by improvements in deposition technology and more importantly due to the development of lithographic techniques and equipment such as X-ray lithography and electron beam lithography. Techniques such as electron beam lithography, X-ray lithography and ion beam lithography, all have advantages in terms of resolution achieved, however, there are disadvantages associated with cost, optics and detrimental effects on the substrate. These methods are currently under investigation to improve upon current lithography process used in the IC industry. With continuous developments in these technologies, it is highly likely that the transition from micro technology or nanotechnology will generate a whole new generation of exciting products and features.

Let us take an example of a demonstration of how several techniques can be combined together to form a 'nano' wine glass

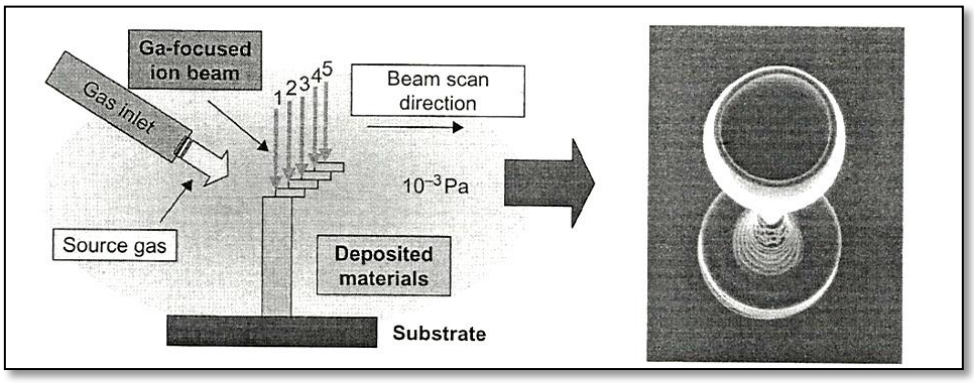


Figure-1.5.Demonstration of three dimensional nanostructure fabrications

In this example, a focused ion beam and CVD have employed to produce this striking nanostructure. The top-down approach is being used to coat various coatings to give improved functionality. For example, vascular stents are being coated using CVD technology

with ultra-thin diamond-like carbon coatings in order to improve biocompatibility and blood flow.

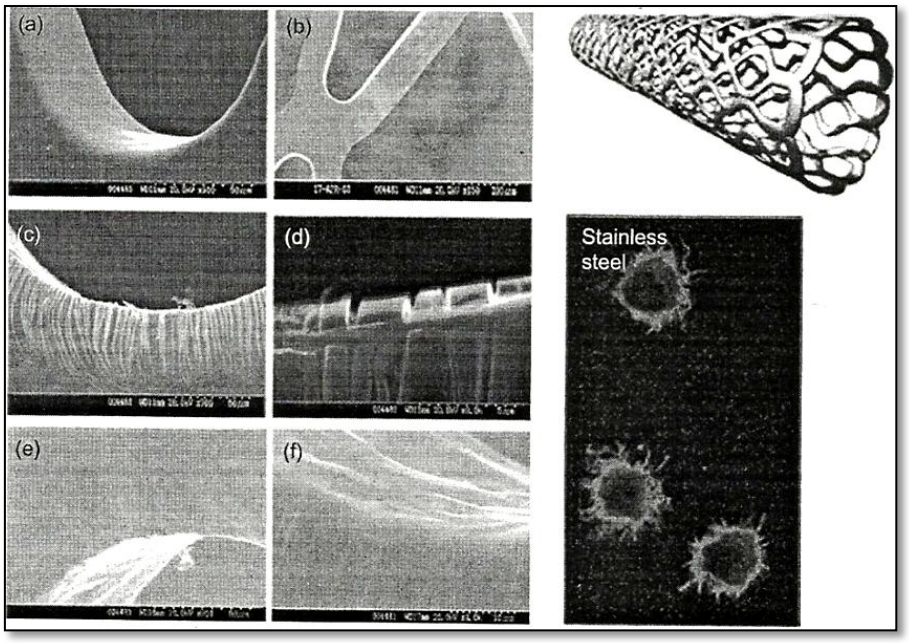


Figure-1.6.Example of stents coated with diamond-like carbon using plasma enhanced CVD Graded a-SixCy: H interfacial layers results in greatly reduced cracking and enhanced adhesion.

1.3.2. Bottom-up approaches

These seek to arrange smaller components into more complex assemblies.

- DNA nanotechnology utilizes the specificity of Watson–Crick base pairing to construct well-defined structures out of DNA and other nucleic acids.
- Approaches from the field of "classical" chemical synthesis (inorganic and organic synthesis) also aim at designing molecules with well-defined shape, e.g. bis-peptides **[17].**
- 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.
- Atomic force microscope tips can be used as a nanoscale "write head" to deposit a chemical upon a surface in a desired pattern in a process called dip pen nanolithography. This technique fits into the larger subfield of nanolithography.

The bottom-up approach involves the fabrication of device structure via systematic assembly of atoms, molecules or other basic units of matter. This is the approach nature uses to repair cells, tissues, organs of living and organ systems in living things, and indeed for life processes such as protein synthesis. Tools are evolving which will give scientists more control over the synthesis and characterization of novel nanostructures and yield a range of new products in the near future. The bottom-up approach involves making nanostructure and devices by arranging atom by atom. The scanning tunnelling microscope (STM) has been used to build nano-sized atomic features such as the letters IBM written using xenon atoms on nickel.

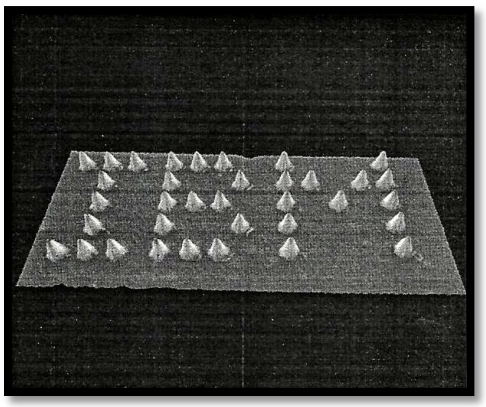


Figure-1.7.Positioning single atom with an STM

While this is beautiful and exciting, it remains that the experiment was carried out under carefully controlled conditions, that is liquid helium cooling and high vacuum, and it took approximately 24 hours to get the letters right. Also the atoms are not bonded to the surface just adsorbed and a small change in temperature or pressure will dislodge them. Since this demonstration significant advances have made in nano-manufacturing. The discovery of STM's ability to image variations in the density distribution of surface-state electrons created in the artists a compulsion to have complete control of not only the atomic landscape, but also the electronic landscape.

1.3.2.1. Atom Manipulation

Single atom manipulation can be achieved with appropriate selection of the charge (polarity), the magnitude and duration of a voltage pulse applied between the STM tip and the sample surface, as well as the tip-to-sample separation. By placing a tungsten tip above silicon atoms and applying voltages of -5.5 V to the surface for 30 ms, silicon atoms can be lifted from the surface,

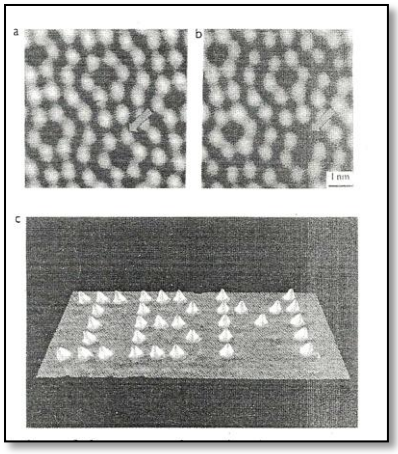


Figure-1.8.a) Manipulation of silicon atoms on a surface before removal, and b) after removal of an atom, Huang D (2001) Artificial atomic surfaces created with STM angle-atom manipulation, microscopy and analysis. C) IBM advertisement made of xenon atoms.

The method can also be selective. Hydrogen can be removed from hydrogen silicon bonds by scanning a tip over the surface while applying a continuous potential difference of several volts, or by applying rapid pulses. The mechanism of extraction in stable and depends on whether the sample is positively or negatively charged. When the sample is positively charged the electrons are involved in breaking the bond, since they are transferred. When the sample is negatively charged a strong electric field is created between the sample and the surface. This field is great enough to pull the bond apart. Atoms can also be deposited once they have been lifted. **Figure-1.8.b** shows a very famous experiment in which atoms were deposited to spell out the smallest advertisement in the world for IBM using xenon atoms. The smallest counting device, an abacus, has been made out of xenon atoms. These atoms are called ad atoms, but molecules can be used as well. Carbon monoxide molecules have been used to make a pictorial man. Nevertheless, if the moving of atoms or molecules could be sped up, it could be used as a mechanism for storing numbers. Atoms have also been moved into a straight line, but probably the most astounding picture is the assembly of iron atoms in a circle so that the wave pattern of the electrons between them can be observed. The corral shows the wave nature of the electrons on the metal surface, rather like the concentric rings you obtain in a cup of tea when you shake it. The wave behaviour of electrons can be explored in other ways. Scientists have been able to create an atomic mirage. An ellipsoid bowl has two radii at each end due to two parts of circles that complete its structure. When water is placed in an ellipsoid bowl and a drip allowed to fall at one of the two centres of radium, that is, the first focal point, then waves move out to the edge, rebound and refocus at the second radius – that is, at the second focal point. Thus the drip can be seen to appear at the second focal point. Thus the drip can be seen to appear at the second radius focal point as a small crest.

The phenomenon is not unique. It is similar to the way in which light is focused by optical lenses or mirrors. What is new is that this is also true for electrons. If an ellipse of atoms is formed and if further atoms are placed at the radius of one ellipse, electrons are added to the pool. They appear at the second radius focal point, like in the water experiment! In effect there is a mirage of the atom the size and shape of the elliptical corral determines the energy and spatial distribution of the confined electrons. These effects are observed because the corral is of a size that is similar to the de Broglie wavelength of the electron, while the water analogy above is good, the phenomenon is a quantum one, and hence drawing an analogy with light (electromagnetic radiation) is a better way of understanding it. The properties of light are transferred when it is refocused. A property of atoms which relates to their magnetic moment is a phenomenon called ‘Kondo resonance’.

By positioning a cobalt (Co) atom, at one radius of the ellipse, a strong Kondo signature is detected at the second radius focus. If we regard the atom as matter rather than electromagnetic radiation then this begs the question: is it an image or really a ‘reformed’ atom? Atoms are, after all, primarily electron waves and nuclei. Whatever the answer, the same electronic states in the surface electrons at the mirage are those surrounding the introduced atom. This is a fundamentally new way of transferring information. It transfers

electrons on the atomic scale but uses the wave nature of electrons instead of conventional wiring and hence has electronic implications.

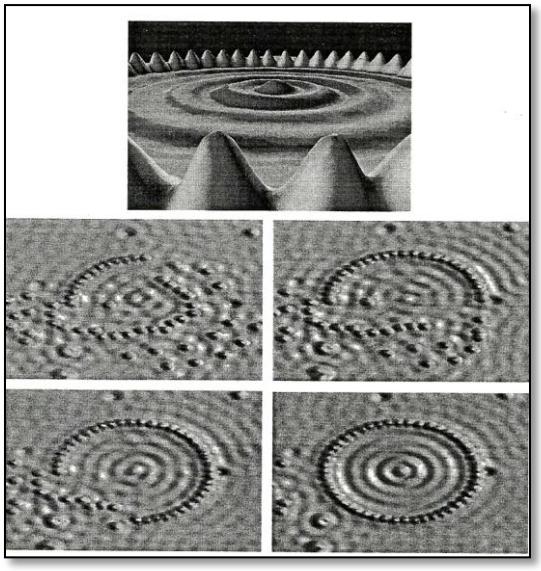


Figure-1.9.Confinement of electrons to quantum corrals on a metal surface.

Fig shows 48 iron atoms positioned into a circular ring in order to 'corral' some surface-state electrons and force them into 'quantum' states of the circular structure. The ripples in the ring of atoms are the density distribution of a particular set of quantum states of corral. The artists were delighted to discover that they could predict what goes on in the corral by solving the classic eigenvalue problem in quantum mechanics – a particle in hard-wall box. Probably, the most publicized material in recent years has been carbon nanotubes. Carbon nanotubes long, thin cylinders of carbon – were discovered in 1991 by S. Iijima. These are large macromolecules that are unique for their size, shape and remarkable physical properties. They can be thought of as a sheet of graphite (a hexagonal lattice of carbon) rolled into a cylinder. These intriguing structures have sparked much excitement in the recent years and large amount of research has been dedicated to their understanding. Currently, the physical properties are still being discovered and disputed. What makes it so difficult is that nanotubes have a very broad range of electronic, thermal and structural properties that change depending on the different kinds of nanotubes (defined by its diameter, length and chirality, or twist). To make things more interesting besides having a single cylindrical wall (SWNTs), nanotubes can have multiple walls (MWNTs) – cylinders inside the order cylinders.

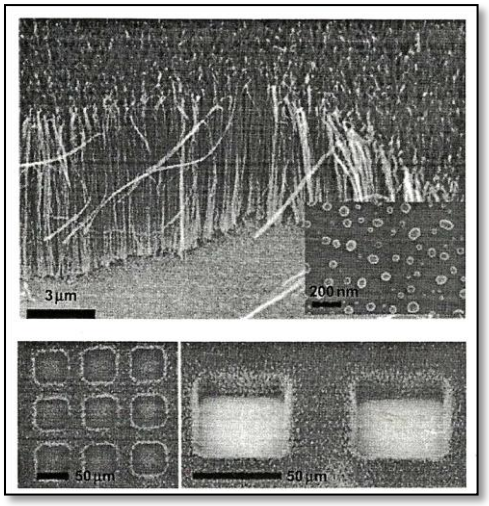


Figure-1.10.Multiwalled carbon nanotubes with a diameter of 30nm and a length of 20µm have been formed within 2 minutes.

Several researchers have grown vertically aligned carbon nanotubes using a microwave plasma-enhanced CVD system using a thin-film cobalt catalyst at 825^0C. The chamber pressure used was 20 Torr. The plasma was generated using hydrogen which was replaced completely with ammonia and acetylene at a total flow rate of 200 sccm.

Note:-Progress in both approaches has been accelerated in recent years with the development and application of highly sensitive equipment. For example, instrument such as atomic force microscope (AFM), scanning tunnelling microscope (STM), electron beam lithography, molecular beam epitaxial, etc., have become available to push forward development in this exciting new field. These instruments allow observation and manipulation of novel nanostructures. Considerable research is being carried throughout the world in development nanotechnology, and many new applications have emerged. However, a related term is nanomanufacturing, used to describe industrial scale manufacture of nanotechnology-based objects at high rate, low cost and reliability. Tools, templates and processes are currently being development that will enable high volume manufacturing of components and structures on a development of commercial products and enable the creations of a new generation of applications in various different commercial sectors including drug delivery, cosmetics, biomedical implants, electronics, and optical components, automotive and aerospace parts.

1.3.3. Functional approaches

These seek to develop components of a desired functionality without regard to how they might be assembled.

- Molecular scale electronics seeks to develop molecules with useful electronic properties. These could then be used as single-molecule components in a nanoelectronic device **[18].**
- Synthetic chemical methods can also be used to create synthetic molecular motors, such as in a so-called nanocar.

1.3.4. Bio mimetic approaches

- Bionics or bio mimicry seeks to apply biological methods and systems found in nature, to the study and design of engineering systems and modern technology. Bio mineralization is one example of the systems studied
- Bio nanotechnology is the use of bio molecules for applications in nanotechnology, including use of viruses. **[19]** Nanocellulose is a potential bulk-scale application.

1.4. Speculative

These subfields seek to anticipate what inventions nanotechnology might yield, or attempt to propose an agenda along which inquiry might progress. These often take a big-picture view of nanotechnology, with more emphasis on its societal implications than the details of how such inventions could actually be created.

- Molecular nanotechnology is a proposed approach which involves manipulating single molecules in finely controlled, deterministic ways. This is more theoretical than the other subfields and is beyond current capabilities.
- Nanorobotics centres on self-sufficient machines of some functionality operating at the nanoscale. There are hopes for applying nanorobots in medicine, **[20, 21, and 22]** but it may not be easy to do such a thing because of several drawbacks of such devices**. [23]** Nevertheless, progress on innovative materials and methodologies has been demonstrated with some patents granted about new nanomanufacturing devices for future commercial applications, which also progressively helps in the development towards nanorobots with the use of embedded nanobioelectronics concepts**. [24, 25]**
- Productive nanosystems are "systems of nanosystems" which will be complex nanosystems that produce atomically precise parts for other nanosystems, not necessarily using novel nanoscale-emergent properties, but well-understood fundamentals of manufacturing. Because of the discrete (i.e. atomic) nature of matter and the possibility of exponential growth, this stage is seen as the basis of another industrial revolution. Mihail Roco, one of the architects of the USA's National Nanotechnology Initiative, has proposed four states of nanotechnology that seem to parallel the technical progress of the Industrial Revolution, progressing from passive nanostructures to active nanodevices to complex nanomachines and ultimately to productive nanosystems.
- Programmable matter seeks to design materials whose properties can be easily, reversibly and externally controlled though a fusion of information science and materials science.
- Due to the popularity and media exposure of the term nanotechnology, the words picotechnology and femtotechnology have been coined in analogy to it, although these are only used rarely and informally.

1.5. Fundamental concepts

Nanotechnology is the engineering of functional systems at the molecular scale. This covers both current work and concepts that are more advanced. In its original sense, nanotechnology refers to the projected ability to construct items from the bottom up, using techniques and tools being developed today to make complete, high performance products. One nanometre (nm) is one billionth, or 10^{-9}, of a meter. By comparison, typical carbon-carbon bond lengths, or the spacing between these atoms in a molecule, are in the range 0.12–0.15 nm, and a DNA double-helix has a diameter around 2 nm. On the other hand, the smallest cellular life-forms,

the bacteria of the genus Mycoplasma, are around 200 nm in length. By convention, nanotechnology is taken as the scale range 1 to 100 nm following the definition used by the National Nanotechnology Initiative in the US. The lower limit is set by the size of atoms (hydrogen has the smallest atoms, which are approximately a quarter of an nm diameter) since nanotechnology must build its devices from atoms and molecules. The upper limit is more or less arbitrary but is around the size that phenomena not observed in larger structures start to become apparent and can be made use of in the nano device.**[8]** These new phenomena make nanotechnology distinct from devices which are merely miniaturised versions of an equivalent macroscopic device; such devices are on a larger scale and come under the description of micro technology.**[9]** To put that scale in another context, the comparative size of a nanometre to a meter is the same as that of a marble to the size of the earth.**[10]** Or another way of putting it: a nanometre is the amount an average man's beard grows in the time it takes him to raise the razor to his face **[10]**.Two main approaches are used in nanotechnology. In the "bottom-up" approach, materials and devices are built from molecular components which assemble themselves chemically by principles of molecular recognition. In the "top-down" approach, nano-objects are constructed from larger entities without atomic-level control **[11]**. Areas of physics such as nanoelectronics, nanomechanics, nanophotonics and nanoionics have evolved during the last few decades to provide a basic scientific foundation of nanotechnology.

1.5.1. Larger to smaller: a materials perspective

A number of physical phenomena become pronounced as the size of the system decreases. These include statistical mechanical effects, as well as quantum mechanical effects, for example the “quantum size effect” where the electronic properties of solids are altered with great reductions in particle size. This effect does not come into play by going from macro to micro dimensions. However, quantum effects become dominant when the nanometre size range is reached, typically at distances of 100 nanometres or less, the so called quantum realm. Additionally, a number of physical (mechanical, electrical, optical, etc.) properties change when compared to macroscopic systems. One example is the increase in surface area to volume ratio altering mechanical, thermal and catalytic properties of materials. Diffusion and reactions at nanoscale, nanostructures materials and nanodevices with fast ion transport are generally referred to nanoionics. Mechanical properties of nanosystems are of interest in the nanomechanics research. The catalytic activity of nanomaterial also opens potential risks in their interaction with biomaterials.

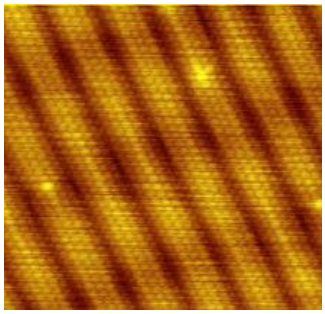


Figure-1.11.Image of reconstruction on a clean Gold (100) surface

As visualized using scanning tunnelling microscopy. The positions of the individual atoms composing the surface are visible.

Materials reduced to the nanoscale can show different properties compared to what they exhibit on a macro scale, enabling unique applications. For instance, opaque substances become transparent (copper); stable materials turn combustible (aluminium); insoluble materials become soluble (gold). A material such as gold, which is chemically inert at normal scales, can serve as a potent chemical catalyst at nanoscales. Much of the fascination with nanotechnology stems from these quantum and surface phenomena that matter exhibits at the nanoscale**. [12]**

1.5.2. Simple to complex: a molecular perspective

Modern synthetic chemistry has reached the point where it is possible to prepare small molecules to almost any structure. These methods are used today to manufacture a wide variety of useful chemicals such as pharmaceuticals or commercial polymers. This ability raises the question of extending this kind of control to the next-larger level, seeking methods to assemble these single molecules into supramolecular assemblies consisting of many molecules arranged in a well defined manner. These approaches utilize the concepts of molecular self-assembly and/or supramolecular chemistry to automatically arrange themselves into some useful conformation through a bottom-up approach. The concept of molecular recognition is especially important: molecules can be designed so that a specific configuration or arrangement is favoured due to non-covalent intermolecular forces. The Watson–Crick base pairing rules are a direct result of this, as is the specificity of an enzyme being targeted to a single substrate, or the specific folding of the protein itself. Thus, two or more components can be designed to be complementary and mutually attractive so that they make a more complex and useful whole. Such bottom-up approaches should be capable of producing devices in parallel and be much cheaper than top-down methods, but could potentially be overwhelmed as the size and complexity of the desired assembly increases. Most useful structures require complex and thermodynamically unlikely arrangements of atoms. Nevertheless, there are many examples of self-assembly based on molecular recognition in biology, most notably Watson–Crick base pairing and enzyme-substrate interactions. The challenge for nanotechnology is whether these principles can be used to engineer new constructs in addition to natural ones.

1.6. Molecular nanotechnology: a long-term view

Molecular nanotechnology, sometimes called molecular manufacturing, describes engineered nanosystems (nanoscale machines) operating on the molecular scale. Molecular nanotechnology is especially associated with the molecular assembler, a machine that can produce a desired structure or device atom-by-atom using the principles of mechanosynthesis. Manufacturing in the context of productive nanosystems is not related to, and should be clearly distinguished from, the conventional technologies used to manufacture nanomaterial such as carbon nanotubes and nanoparticles. When the term "nanotechnology" was independently coined and popularized by Eric Drexler (who at the time was unaware of an earlier usage by Norio Taniguchi) it referred to a future manufacturing technology based on molecular machine systems. The premise was that molecular scale biological analogies of traditional machine components demonstrated molecular machines were possible: by the countless examples found in biology, it is known that sophisticated, stochastically optimised biological machines can be produced. It is hoped that developments in nanotechnology will make possible their construction by some other means, perhaps using bio mimetic principles. However, Drexler and other researchers have proposed that advanced nanotechnology,

although perhaps initially implemented by bio mimetic means, ultimately could be based on mechanical engineering principles, namely, a manufacturing technology based on the mechanical functionality of these components (such as gears, bearings, motors, and structural members) that would enable programmable, positional assembly to atomic specification. The physics and engineering performance of exemplar designs were analyzed in Drexler's book Nanosystems. In general it is very difficult to assemble devices on the atomic scale, as all one has to position atoms on other atoms of comparable size and stickiness. Another view, put forth by Carlo Montemagno, is that future nanosystems will be hybrids of silicon technology and biological molecular machines. Yet another view, put forward by the late Richard Smalley, is that mechanosynthesis is impossible due to the difficulties in mechanically manipulating individual molecules. This led to an exchange of letters in the ACS publication Chemical & Engineering News in 2003. Though biology clearly demonstrates that molecular machine systems are possible, non-biological molecular machines are today only in their infancy. Leaders in research on non-biological molecular machines are Dr. Alex Zettl and his colleagues at Lawrence Berkeley Laboratories and UC Berkeley. They have constructed at least three distinct molecular devices whose motion is controlled from the desktop with changing voltage: a nanotube nanomotor, a molecular actuator, **[13]** and a nanoelectromechanical relaxation oscillator. **[14]** See nanotube nanomotor for more examples. An experiment indicating that positional molecular assembly is possible was performed by Ho and Lee at Cornell University in 1999. They used a scanning tunnelling microscope to move an individual carbon monoxide molecule (CO) to an individual iron atom (Fe) sitting on a flat silver crystal, and chemically bound the CO to the Fe by applying a voltage.

1.7. Nanomaterial

Nanomaterial and nanotechnologies attract tremendous attention in recent research work. New physical properties and new technologies both in sample preparation and device fabrication evoke on account of the development of nanoscience. Nanotechnology is already an economic reality. The diversity and complexity of manufactured nanomaterial are continuously increasing: we are facing a fast growing, very heterogeneous class of materials which demand attention.

Their unique characteristics that are in the first place related to their small sizes lead to important scientific and technological innovations in various sectors, but there are legitimate concerns that the same characteristics may cause new risks, that cannot always be assessed by the classical tools. Nanomaterial' means a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimension is in the size range 1 nm-100 nm. The occurrence of matter in nana dimensions comes with properties (chemical, mechanical, optical, etc.) often unexpected and completely different from those of the same materials at the micro- or macro-scale. In addition, nanomaterial comes in a wide variety of shapes: spherical particles, nanotubes, nanofibers, nanowires.

Nanomaterial are now a major economic and technological opportunity for companies worldwide. Nanomaterial have an increasing impact in the new and emerging industries such as aerospace, computer, electronics and renewable energy, as well as in traditional industries such as food, cosmetics, automotive and construction. There are numerous applications: drug delivery, anti-scratch paint, transparent sunscreens, more durable tires, anti-bacterial clothes, self-cleaning concrete, etc. A large number of employees are already being exposed to

nanomaterial, both in research laboratories, production facilities or downstream user companies.

1.7.1. General attributes of nanomaterial

Proper identification of nanomaterial attributes is critically important when comparing various Alternative nanomaterials. Therefore, whenever a nanomaterial user goes to the supplier for purchase of new nanomaterial, this identification of attributes attain significant importance. Sometimes mere articulation of what attributes are important in the context of particular alternatives under consideration can lead to a rational choice without formal application of some quantitative or semi-quantitative methodology. However, in most cases the user needs to be assisted in identifying the nanomaterial attributes wisely and accordingly the application. The final product of industry will directly depend on the proper choice of the nanomaterial. So the nanomaterial should be selected with proper identification of attributes. If the nanomaterial attributes identification is done carefully, the selection of the nanomaterial for particular application will be precise, which will boost the productivity

Here some of the general attributes that needs to be considered for manufacturing, designing and selection of appropriate nanomaterial is summarised in a tabular form as shown below.

1.Small size	2.Very large surface area to volume ratio
3.Spatial confinement	4.High young's modulus
5.Improve adhesion	6.Durability
7.Abrasion resistance	8.Extreme high thermal conductivity
9.Reduced imperfections	10.High surface energy
11.Structural design	12.Magnetism
13.Quantum effects	14.Single electron effects
15.Size dependent effects	

Table-1.1.General attributes of Nanomaterial

1.7.2. General properties of Nanomaterial

Thermal Properties & Magnetic Properties	Optical Properties	Electrical Properties	Mechanical Properties
Magnetic material	Index of refraction	Electrical conductivity	Bulk metallic
Super-magnetic material	Quantum confinement	Photoconductivity	Influence of porosity
Susceptibility	Quantum dots	Electrical resistivity	Electrical performance
Thermal conductivity	Laser	Dielectric strength	Superconductivity
Thermal expansion	Phosphor	Curvature effects	Conductance quantization
Thermal stability	Imaging	Electrical performance	Band gap
Thermal source	Photo catalysis	Superconductivity	Electrical conductivity
Coefficient of thermal expansion	Photoelectron chemistry	Conductance quantization	Percentage elongation
Ballistic conductance	Absorption	Electrical conductivity	Internal surface area
Temperature stability	Photo-luminescence		Specific strength
Phonon mean free path	Surface Plasmon		Fracture toughness
Relaxation time	Oscillation		Super-plasticity

Table-1.2.General properties of Nanomaterial

1.7.3. Characteristics of nanomaterial

Nanomaterial can be characterised as;-

- Materials that is nano-structured in the bulk.
- Materials that have nano-structured on the surface.
- Materials that contain nano-structured particle.

Nanomaterials can be characterised by characterization techniques which are given as follows:-

- X-ray and Electron diffraction (XRD, XRED)
- Electron microscopy (EM)
- Scanning transmission electron microscope (STEM)
- Optical spectroscopy
  a) UV-VIS spectroscopy
  b) Absorption and photoluminescence

c) Raman spectroscopy

- Optical microscope
- Atomic force microscopy (AFM)
- Scanning tunnelling microscope (STM)
- Transmission electron microscope (TEM)
- Scanning electron microscope (SEM)
- High resolution transmission electron microscope (HRTEM)

Out of all these some of the most important techniques are discussed in the later section under Methods and Techniques.

1.7.4. Applications of Nanomaterial

The nanomaterial field includes subfields which develop or study materials having unique properties arising from their nanoscale dimensions. **[16]**

- Interface and colloid science has given rise to many materials which may be useful in nanotechnology, such as carbon nanotubes and other fullerenes, and various nanoparticles and nanorods. Nanomaterial with fast ion transport is related also to nanoionics and nanoelectronics.
- Nanoscale materials can also be used for bulk applications; most present commercial applications of nanotechnology are of this flavour.
- Progress has been made in using these materials for medical applications; see Nanomedicine.
- Nanoscale materials are sometimes used in solar cells which combats the cost of traditional Silicon solar cells
- Development of applications incorporating semiconductor nanoparticles to be used in the next generation of products, such as display technology, lighting, solar cells and biological imaging; see quantum dots.

1.8. Methods and techniques

1.8.1. Lithographic Methods

Lithographic methods are important for micro- and nanofabrication. Lithography is the art of drawing or writing on a kind of yellow salty limestone so that impressions in ink can be taken, in the Oxford Dictionary the word ‘lithos’ comes from Greek for stone.

In micro- and nanofabrication we mean pattern transfer. Owing to limitations in current photolithographic processes, there is a challenge to develop novel lithographic processes with better resolution for smaller features. One such development is that of Dip-pen nanolithography (DPN). Dip-pin technology, in which ink on a pointed object is transported to a surface via capillary forces, is approximately 4000 years old. The difference with DPN is that the pointed object has a tip which has been sharpened to a few atoms across in some cases.

DPN is a scanning probe nano patterning technique in which an atomic force microscope (AFM) tip is used to deliver molecules to a surface via a solvent meniscus, which naturally

forms in the ambient atmosphere. It is a direct write technique and is reported to give high-resolution patterning capabilities for a number of molecular and bio molecular 'inks' on a variety of substrates such as metals, semiconductor and monolayer functionalized surfaces.

DPN allows one to precisely pattern multiple patterns with good registration. It's both a fabrication and imaging tool, as the patterned areas can be imaged with clean or ink-coated tips. The ability to achieve precise alignment of multiple patterns is an additional advantage earned by using an AFM tip to write as well as read nano scopic features on a surface. These attributes make DPN a valuable tool for studying fundamental issues in colloid chemistry, surface science and nanotechnology.

For instance, diffusion and capillarity on a surface at the nano meter level, organization and crystallization of particles onto chemical or bio molecular templates, monolayer etching resists for semiconductor and nanometre sized tethered polymer structures can be investigated using this technique. In order to create stable nanostructures, it's beneficial to use molecules that can anchor themselves to the substrate via chemisorptions or electrostatic interactions. When alkane thiols are patterned on a gold substrate, a monolayer is formed in which the thiol head groups from relatively strong bonds to the gold and the alkane chains extend roughly perpendicular to the surface.

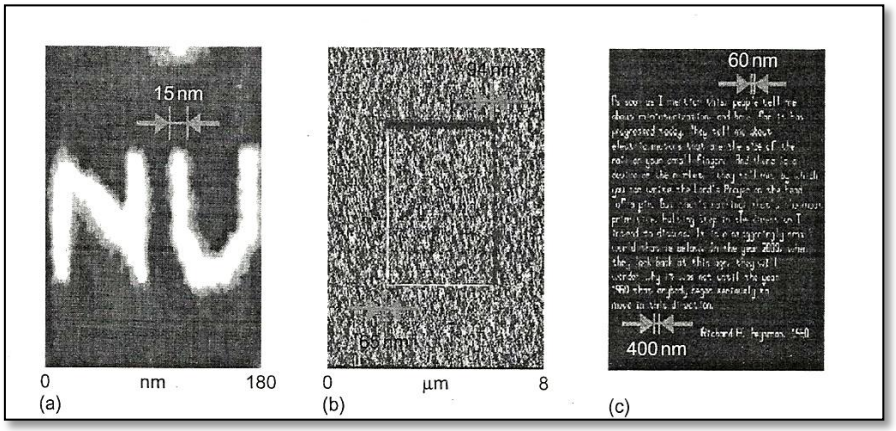


Figure-1.12

a) Ultra high resolution pattern of mercaptohexadecanoic acid in automatically flat gold surface.

b) DPN-generated multi component nanostructure with two aligned alkanethiol patterns.

c) Richard Feynman's historic speech written using the DPN nanoplotter.

Creating nanostructure using DPN is a single step process that does not require the use of resists. Using a conventional AFM, DPN has been reported to achieve ultra-high resolution features with line widths as small as 10 - 15 nm with ~5 nm spatial resolutions.

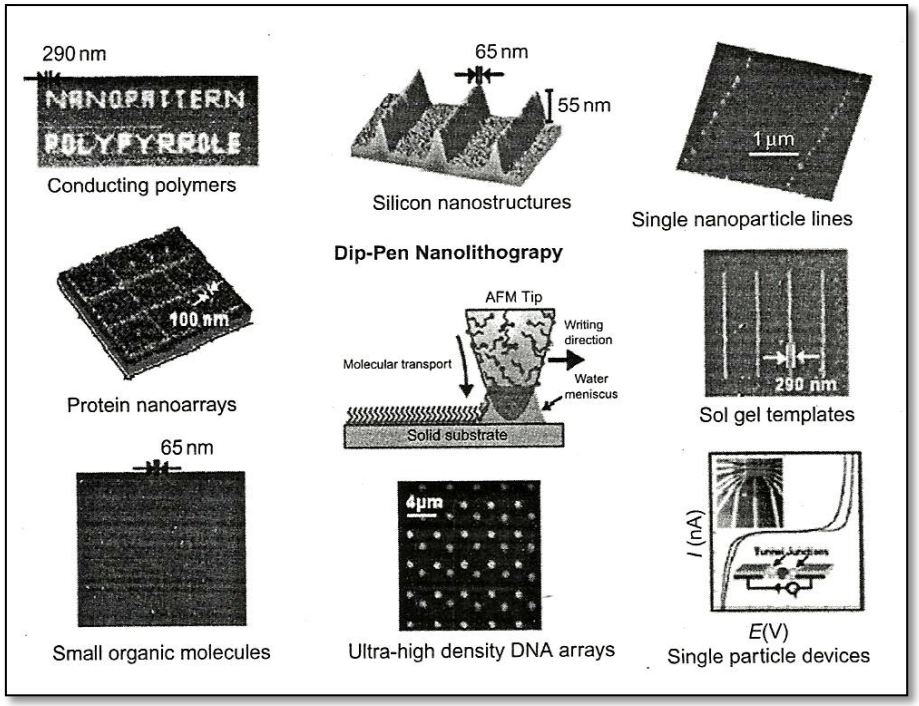


Figure-1.13. some of the potential applications of DPN.

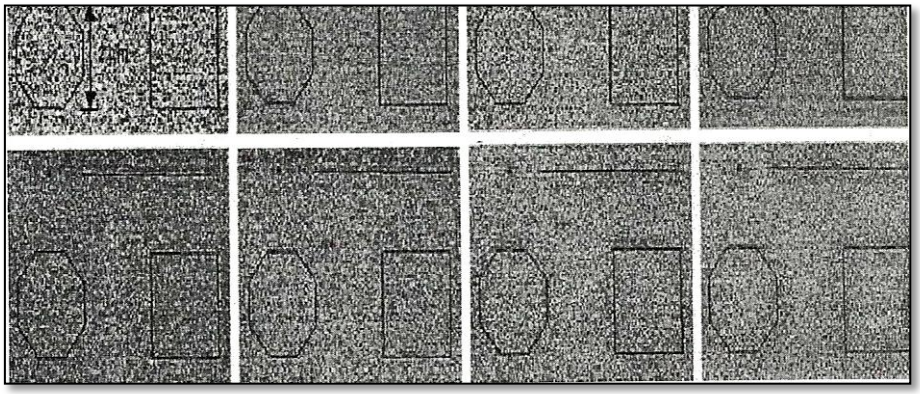


Figure-1.14.LFM images of nanolithography patterns which were formed using an eight-pen nanoplotter capable of doing parallel DPN

1.8.2. Lithographic Techniques

For nanotechnological applications, it is not only important to pattern molecules in high resolution, but also to functionalize surfaces with patterns of two or more components. There are several important modern developments. The atomic force microscope (AFM) and the Scanning Tunnelling 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 co-workers in the 1970s, that made it possible to see structures at the nanoscale

1.8.2.1. Lithographic Techniques used to "Measure the Topology of Nanostructures"

1.8.2.1.1. Scanning Electron Microscope

A scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition, and other properties such as electrical conductivity. The types of signals produced by an SEM include secondary electrons, back-scattered electrons (BSE), characteristic X-rays, light (cathodo-luminescence), specimen current and transmitted electrons.

Secondary electron detectors are common in all SEMs, but it is rare that a single machine would have detectors for all possible signals. The signals result from interactions of the electron beam with atoms at or near the surface of the sample. In the most common or standard detection mode, secondary electron imaging or SEI, the SEM can produce very high-resolution images of a sample surface, revealing details less than 1 nm in size. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample.

This is exemplified by the micrograph of pollen shown to the right. A wide range of magnifications is possible, from about 10 times (about equivalent to that of a powerful hand-lens) to more than 500,000 times, about 250 times the magnification limit of the best light microscopes. Back-scattered electrons (BSE) are beam electrons that are reflected from the sample by elastic scattering. BSE are often used in analytical SEM along with the spectra made from the characteristic X-rays. Because the intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen, BSE images can provide information about the distribution of different elements in the sample.

For the same reason, BSE imaging can image colloidal gold immuno-labels of 5 or 10 nm diameters, which would otherwise be difficult or impossible to detect in secondary electron images in biological specimens. Characteristic X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher energy electron to fill the shell and release energy. These characteristic X-rays are used to identify the composition and measure the abundance of elements in the sample.

History

The first SEM image was obtained by Max Knoll, who in 1935 obtained an image of silicon steel showing electron channelling contrast. Further pioneering work on the physical principles of the SEM and beam specimen interactions was performed by Manfred von Ardenne in 1937, which produced a British patent but never made a practical instrument. The SEM was further developed by Professor Sir Charles Oakley and his postgraduate student Gary Stewart and was first marketed in 1965 by the Cambridge Scientific Instrument Company as the "Stereos can". The first instrument was delivered to DuPont.

Scanning process and image formation

In a typical SEM, an electron beam is thermionic ally emitted from an electron gun fitted with a tungsten filament cathode. Tungsten is normally used in thermionic electron guns because it 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 (LaB_6) cathodes, which can be used in a standard tungsten filament SEM if the vacuum system is upgraded 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.

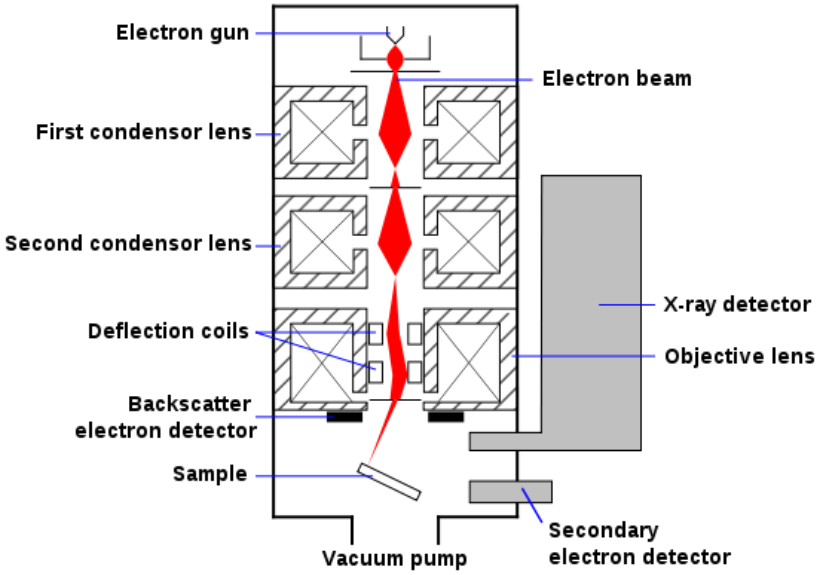


Figure-1.15.Schematic diagram of an SEM.

The electron beam, which typically has an energy ranging from 0.2 keV to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the x and y axes so that it scans in a raster fashion over a rectangular area of the sample surface.

Working

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 around 5 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 electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized 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, which are displayed as variations in brightness on a cathode ray tube. The raster scanning of the CRT display is synchronised with that of the beam on the specimen in the

microscope, and the resulting image is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen. The image may be captured by photography from a high-resolution cathode ray tube, but in modern machines is digitally captured and displayed on a computer monitor and saved to a computer's hard disk.

Magnification

Magnification in a SEM can be controlled over a range of up to 6 orders of magnitude from about 10 to 500,000 times. Unlike optical and transmission electron microscopes, image magnification in the SEM is not a function of the power of the objective lens. SEMs may have condenser and objective lenses, but their function is to focus the beam to a spot, and not to image the specimen. Provided the electron gun can generate a beam with sufficiently small diameter, a SEM could in principle work entirely without condenser or objective lenses, although it might not be very versatile or achieve very high resolution.

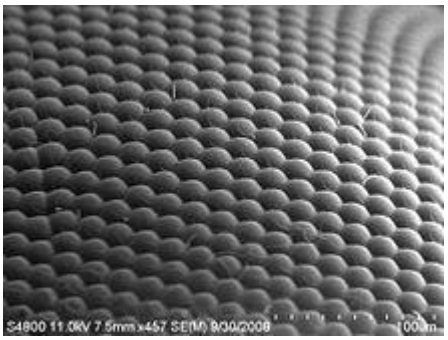


Figure-1.16.An SEM micrograph of a house fly compound eye surface at 450× magnification.

In a SEM, as in scanning probe microscopy, magnification results from the ratio of the dimensions of the raster on the specimen and the raster on the display device. Assuming that the display screen has a fixed size, higher magnification results from reducing the size of the raster on the specimen, and vice versa. Magnification is therefore controlled by the current supplied to the x, y scanning coils, or the voltage supplied to the x, y deflector plates, and not by objective lens power.

Resolution

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 that 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) transmission electron microscope (TEM).

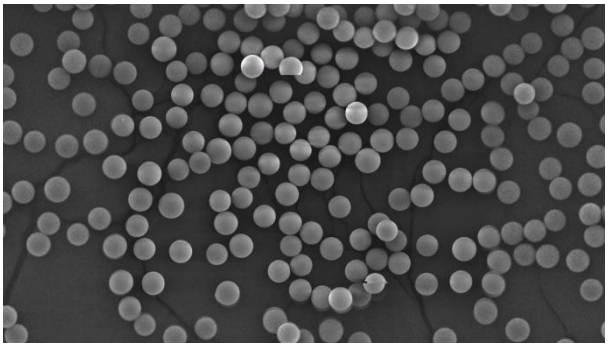


Figure-1.17.A video illustrating a typical practical magnification range of a scanning electron microscope designed for biological specimens. The video starts at 25x, about 6 mm across the whole field of view, and zooms in to 12000x, about 12 µm across the whole field of view. The spherical objects are glass beads with a diameter of 10 µm, similar in diameter to a red blood cell.

The SEM has compensating advantages, though, including the ability to image a comparatively large area of the specimen; the ability to image bulk materials (not just thin films or foils); and the variety of analytical modes available for measuring the composition and properties of the specimen. 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. At low-beam energies, the best resolution (by 2009) is achieved by the Magellan XHR system from FEI Company (0.9 nm at 1 kV).

Sample Preparation

All samples must also be of an appropriate size to fit in the specimen chamber and are generally mounted rigidly on a specimen holder called a specimen stub. Several models of SEM can examine any part of a 6-inch (15 cm) semiconductor wafer, and some can tilt an object of that size to 45°.

Figure-1.18.A spider coated in gold, having been prepared for viewing with a scanning electron microscope.

Figure-1.19.13mm radius aluminium stubs (the base to support and prepare a sample on) for sample preparation and gold coating

For conventional imaging in the SEM, specimens must be electrically conductive, at least at the surface, and electrically grounded to prevent the accumulation of electrostatic charge at the surface. Metal objects require little special preparation for SEM except for cleaning and mounting on a specimen stub. Nonconductive specimens tend to charge when scanned by the electron beam, and especially in secondary electron imaging mode, this causes scanning faults and other image artifacts. They are therefore usually coated with an ultrathin coating of electrically conducting material, deposited on the sample either by low-vacuum sputter coating or by high-vacuum evaporation. Conductive materials in current use for specimen coating include gold, gold/palladium alloy, platinum, osmium, iridium, tungsten, chromium, and graphite. Additionally, coating may increase signal/noise ratio for samples of low atomic number (Z). The improvement arises because secondary electron emission for high-Z materials is enhanced.

An alternative to coating for some biological samples is to increase the bulk conductivity of the material by impregnation with osmium using variants of the OTO staining method (O-osmium, T-thiocarbohydrazide, O-osmium). Non-conducting specimens may be imaged uncoated using specialized SEM instrumentation such as the "Environmental SEM" (ESEM) or field emission gun (FEG) SEMs operated at low voltage. Environmental SEM instruments place the specimen in a relatively high-pressure chamber where the working distance is short and the electron optical column is differentially pumped to keep vacuum adequately low at the electron gun. The high-pressure region around the sample in the ESEM neutralizes charge and provides an amplification of the secondary electron signal. Low-voltage SEM of non-conducting specimens can be operationally difficult to accomplish in a conventional SEM and is typically a research application for specimens that are sensitive to the process of applying conductive coatings. Low-voltage SEM of non-conducting specimens can be operationally difficult to accomplish in a conventional SEM and is typically a research application for specimens that are sensitive to the process of applying conductive coatings. Low-voltage SEM is typically conducted in an FEG-SEM because the FEG is capable of producing high primary electron brightness even at low accelerating potentials. Operating conditions to prevent charging of non-conductive specimens must be adjusted such that the incoming beam current was equal to sum of out coming secondary and backscattered electrons currents. It usually occurs at accelerating voltages of 0.5-4 kV.

Embedding in a resin with further polishing to a mirror-like finish can be used for both biological and materials specimens when imaging in backscattered electrons or when doing quantitative X-ray microanalysis.

Materials

Back scattered electron imaging, quantitative X-ray analysis, and X-ray mapping of specimens often requires that the surfaces be ground and polished to an ultra smooth surface. Specimens that undergo WDS or EDS analysis are often carbon coated. In general, metals are not coated prior to imaging in the SEM because they are conductive and provide their own pathway to ground.Fractography is the study of fractured surfaces that can be done on a light microscope or commonly, on an SEM. The fractured surface is cut to a suitable size, cleaned of any organic residues, and mounted on a specimen holder for viewing in the SEM.Integrated circuits may be cut with a focused ion beam (FIB) or other ion beam milling instrument for viewing in the SEM. The SEM in the first case may be incorporated into the FIB.Metals, geological specimens, and integrated circuits all may also be chemically polished for viewing in the SEM.Special high-resolution coating techniques are required for high-magnification imaging of inorganic thin films.

One drawback of SEM is that it cannot be used to analyses specimen that give off any type of vapour. This vapour would interact with the electrons. This disadvantage can be overcome by using cryogenic SEM, where the specimen is frozen and coated with gold so that the vacuum tube can remain relatively free of vapour. In recent years, the SEM has been made with a controlled vacuum chamber, where the top of the chamber is a vacuum, and the very bottom to the chamber near the sample is kept at low vacuum. This allows the natural expulsion of particles from wet samples, so the microscope can analyses crystallizing and drying. A small area of low vacuum does not distort the SEM image significantly. This instrument is called an environmental SEM.

1.8.2.1.2. Environmental Scanning Electron Microscopy

Conventional SEM requires samples to be imaged under vacuum, because a gas atmosphere rapidly spreads and attenuates electron beams. As a consequence, samples that produce a significant amount of vapour, e.g. wet biological samples or oil-bearing rock, must be either dried or cryogenically frozen. Processes involving phase transitions, such as the drying of adhesives or melting of alloys, liquid transport, chemical reactions, and solid-air-gas systems, in general cannot be observed. Some observations of living insects have been possible, however. The first commercial development of the Environmental SEM (ESEM) in the late 1980s allowed samples to be observed in low-pressure gaseous environments (e.g. 1-50 Torr) and high relative humidity (up to 100%). This was made possible by the development of a secondary-electron detector capable of operating in the presence of water vapour and by the use of pressure-limiting apertures with differential pumping in the path of the electron beam to separate the vacuum region (around the gun and lenses) from the sample chamber.

The first commercial ESEMs were produced by the ElectroScan Corporation in USA in 1988. ElectroScan was taken over by Philips (who later sold their electron-optics division to FEI Company) in 1996. ESEM is especially useful for non-metallic and biological materials because coating with carbon or gold is unnecessary. Uncoated Plastics and Elastomers can be routinely examined, as can uncoated biological samples. Coating can be difficult to reverse, may conceal small features on the surface of the sample and may reduce the value of the results obtained. X-ray analysis is difficult with a coating of a heavy metal, so carbon coatings are routinely used in conventional SEMs, but ESEM makes it possible to perform X-

ray microanalysis on uncoated non-conductive specimens. ESEM may be the preferred for electron microscopy of unique samples from criminal or civil actions, where forensic analysis may need to be repeated by several different experts.

Environmental SEM allows use of hydrated specimens, omitting dehydration procedure. The accumulation of electric charge on the surfaces of non-metallic specimens can be avoided by using environmental SEM in which the specimen is placed in an internal chamber at higher pressure, rather than the vacuum in the electron optical column. Positively charged ions generated by beam interactions with the gas help to neutralize the negative charge on the specimen surface. The pressure of gas in the chamber can be controlled, and the type of gas used can be varied according to need. Coating is thus unnecessary. In ESEM mode X-ray analysis is prone to artifacts arose from electron beam scattering on gases of specimen chamber.

Detection of secondary electrons

The most common imaging mode collects low-energy (<50 eV) secondary electrons that are ejected from the k-orbitals of the specimen atoms by inelastic scattering interactions with beam electrons. Due to their low energy, these electrons originate within a few nanometers from the sample surface The electrons are detected by an Everhart-Thornley detector, which is a type of scintillator-photomultiplier system. The secondary electrons are first collected by attracting them towards an electrically biased grid at about +400 V, and then further accelerated towards a phosphor or scintillator positively biased to about +2,000 V. The accelerated secondary electrons are now sufficiently energetic to cause the scintillator to emit flashes of light (cathodoluminescence), which are conducted to a photomultiplier outside the SEM column via a light pipe and a window in the wall of the specimen chamber. The amplified electrical signal output by the photomultiplier is displayed as a two-dimensional intensity distribution that can be viewed and photographed on an analogue video display, or subjected to analog-to-digital conversion and displayed and saved as a digital image. This process relies on a raster-scanned primary beam. The brightness of the signal depends on the number of secondary electrons reaching the detector. If the beam enters the sample perpendicular to the surface, then the activated region is uniform about the axis of the beam and a certain number of electrons "escape" from within the sample. As the angle of incidence increases, the "escape" distance of one side of the beam will decrease, and more secondary electrons will be emitted. Thus steep surfaces and edges tend to be brighter than flat surfaces, which results in images with a well-defined, three-dimensional appearance. Using the signal of secondary electrons image resolution less than 0.5 nm is possible.

Detection of backscattered electrons

Backscattered electrons (BSE) consist of high-energy electrons originating in the electron beam, that are reflected or back-scattered out of the specimen interaction volume by elastic scattering interactions with specimen atoms. Since heavy elements (high atomic number) backscatter electrons more strongly than light elements (low atomic number), and thus appear brighter in the image, BSE are used to detect contrast between areas with different chemical compositions. The Everhart-Thornley detector, which is normally positioned to one side of the specimen, is inefficient for the detection of backscattered electrons because few such electrons are emitted in the solid angle subtended by the detector, and because the positively biased detection grid has little ability to attract the higher energy BSE electrons.

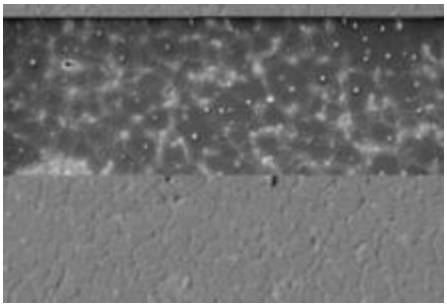


Figure-1.20.Comparison of SEM techniques: Top: backscattered electron analysis – composition Bottom: secondary electron analysis - topography

Dedicated backscattered electron detectors are positioned above the sample in a "doughnut" type arrangement, concentric with the electron beam, maximising the solid angle of collection. BSE detectors are usually either of scintillator or of semiconductor types. When all parts of the detector are used to collect electrons symmetrically about the beam, atomic number contrast is produced. However, strong topographic contrast is produced by collecting back-scattered electrons from one side above the specimen using an asymmetrical, directional BSE detector; the resulting contrast appears as illumination of the topography from that side. Semiconductor detectors can be made in radial segments that can be switched in or out to control the type of contrast produced and its directionality.

Backscattered electrons can also be used to form an electron backscatter diffraction (EBSD) image that can be used to determine the crystallographic structure of the specimen.

Applications of ESEM

1. Beam-injection analysis of semiconductors

The nature of the SEM's probe, energetic electrons, makes it uniquely suited to examining the optical and electronic properties of semiconductor materials. The high-energy electrons from the SEM beam will inject charge carriers into the semiconductor. Thus, beam electrons lose energy by promoting electrons from the valence band into the conduction band, leaving behind holes.In a direct bandgap material, recombination of these electron-hole pairs will result in cathodoluminescence; if the sample contains an internal electric field, such as is present at a p-n junction, the SEM beam injection of carriers will cause electron beam induced current (EBIC) to flow.Cathodoluminescence and EBIC are referred to as "beam-injection" techniques, and are very powerful probes of the optoelectronic behavior of semiconductors, in particular for studying nanoscale features and defects.

2. Cathodoluminescence

Cathodoluminescence, the emission of light when atoms excited by high-energy electrons return to their ground state, is analogous to UV-induced fluorescence, and some materials such as zinc sulfide and some fluorescent dyes, exhibit both phenomena. Cathodoluminescence is most commonly experienced in everyday life as the light emission from the inner surface of the cathode ray tube in television sets and computer CRT monitors. In the SEM, CL detectors either collect all light emitted by the specimen or can analyse the

wavelengths emitted by the specimen and display an emission spectrum or an image of the distribution of cathodoluminescence emitted by the specimen in real colour.

3. X-ray microanalysis

X-rays, which are also produced by the interaction of electrons with the sample, may also be detected in an SEM equipped for energy-dispersive X-ray spectroscopy or wavelength dispersive X-ray spectroscopy.

3D in SEM

3D data can be measured in the SEM with different methods such as:

- Photogrammetry (2 or 3 images from tilted specimen)
- Photometric stereo (use of 4 images from BSE detector)
- Inverse reconstruction using electron-material interactive models[25][26]

Possible applications are roughness measurement, measurement of fractal dimension, corrosion measurement and height step measurement.

1.8.2.1.3. Scanning probe microscopy

Scanning Probe Microscopy (SPM) is a branch of microscopy that forms images of surfaces using a physical probe that scans the specimen. An image of the surface is obtained by mechanically moving the probe in a raster scan of the specimen, line by line, and recording the probe-surface interaction as a function of position. SPM was founded with the invention of the scanning tunneling microscope in 1981. Many scanning probe microscopes can image several interactions simultaneously. The manner of using these interactions to obtain an image is generally called a mode. The resolution varies somewhat from technique to technique, but some probe techniques reach a rather impressive atomic resolution. They owe this largely to the ability of piezoelectric actuators to execute motions with a precision and accuracy at the atomic level or better on electronic command. One could rightly call this family of techniques "piezoelectric techniques". The other common denominator is that the data are typically obtained as a two-dimensional grid of data points, visualized in false color as a computer image.Of these techniques AFM and STM are the most commonly used for roughness measurements.

Probe tips

Probe tips are normally made of platinum/iridium, silicon nitride or gold. There are two main methods for obtaining a sharp probe tip, acid etching and cutting. The first involves dipping a wire end first into an acid bath and waiting until it has etched through the wire and the lower part drops away. The remainder is then removed and the resulting tip is often one atom in diameter. An alternative and much quicker method is to take a thin wire and cut it with a pair of scissors or a scalpel. Testing the tip produced via this method on a sample with a known profile will indicate whether the tip is good or not and a single sharp point is achieved roughly 50% of the time. It is not uncommon for this method to result in a tip with more than one peak; one can easily discern this upon scan due to a high level of ghost images.

Advantages of scanning probe microscopy

- The resolution of the microscopes is not limited by diffraction, but only by the size of the probe-sample interaction volume (i.e., point spread function), which can be as small as a few picometres. Hence the ability to measure small local differences in object height (like that of 135 picometre steps on <100> silicon) is unparalleled. Laterally the probe-sample interaction extends only across the tip atom or atoms involved in the interaction.
- The interaction can be used to modify the sample to create small structures (nanolithography).
- Unlike electron microscope methods, specimens do not require a partial vacuum but can be observed in air at standard temperature and pressure or while submerged in a liquid reaction vessel.

Disadvantages of scanning probe microscopy

- The detailed shape of the scanning tip is sometimes difficult to determine. Its effect on the resulting data is particularly noticeable if the specimen varies greatly in height over lateral distances of 10 nm or less.

- The scanning techniques are generally slower in acquiring images, due to the scanning process. As a result, efforts are being made to greatly improve the scanning rate. Like all scanning techniques, the embedding of spatial information into a time sequence opens the door to uncertainties in metrology, say of lateral spacings and angles, which arise due to time-domain effects like specimen drift, feedback loop oscillation, and mechanical vibration.

- The maximum image size is generally smaller.

- Scanning probe microscopy is often not useful for examining buried solid-solid or liquid-liquid interfaces.

1.8.2.1.4. Atomic Force Microscopy

Atomic force microscopy (AFM) or scanning force microscopy (SFM) is a very high resolution type of scanning probe microscopy, with demonstrated resolution on the order of fractions of a nanometer, more than 1000 times better than the optical diffraction limit. The precursor to the AFM, the scanning tunnelling microscope, was developed by Gerd Binnig and Heinrich Rohrer in the early 1980s at IBM Research - Zurich, a development that earned them the Nobel Prize for Physics in 1986. Binnig, Quate and Gerber invented the first atomic force microscope (also abbreviated as AFM) in 1986. The first commercially available atomic force microscope was introduced in 1989. The AFM is one of the foremost tools for imaging, measuring, and manipulating matter at the nanoscale. The information is gathered by "feeling" the surface with a mechanical probe. Piezoelectric elements that facilitate tiny but accurate and precise movements on (electronic) command enable the very precise scanning. In some variations, electric potentials can also be scanned using conducting cantilevers. In newer more advanced versions, currents can even be passed through the tip to probe the electrical conductivity or transport of the underlying surface, but this is much more challenging with very few research groups reporting reliable data.

Basic principles

The AFM consists of a cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. The cantilever is typically silicon or silicon nitride with a tip radius of curvature on the order of nanometres. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke's law. Depending on the situation, forces that are measured in AFM include mechanical contact force, van der Waals forces, capillary forces, chemical bonding, electrostatic forces, magnetic forces (see magnetic force microscope, MFM), Casimir forces, solvation forces, etc. Along with force, additional quantities may simultaneously be measured through the use of specialized types of probe (see scanning thermal microscopy, scanning joule expansion microscopy, photothermal micro spectroscopy, etc.). Typically, the deflection is measured using a laser spot reflected from the top surface of the cantilever into an array of photodiodes.

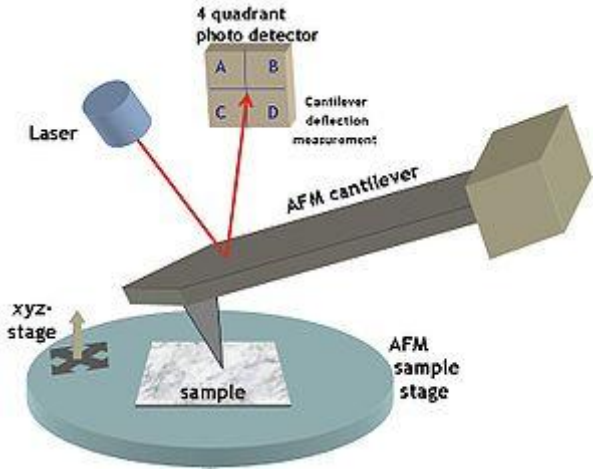
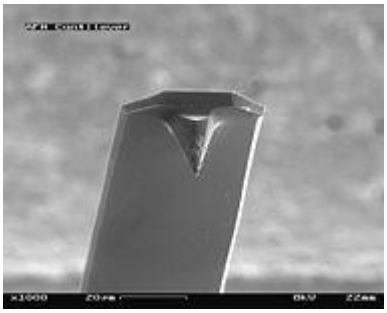


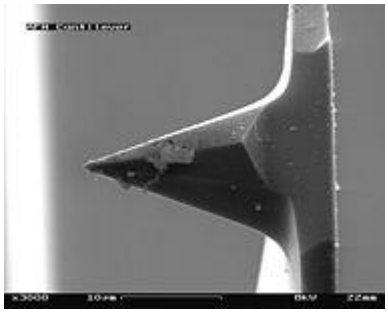
Figure-1.21. Typical AFM setup.

A micro-fabricated 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 photo detectors, allowing the deflection to be measured and assembled into an image of the surface.

Other methods that are used include optical interferometry, capacitive sensing or piezoresistive AFM cantilevers. These cantilevers are fabricated with piezoresistive elements that act as a strain gauge. Using a Wheatstone bridge, strain in the AFM cantilever due to deflection can be measured, but this method is not as sensitive as laser deflection or interferometry.



a)



b)

Figure-1.22. a) Electron micrograph of a used AFM cantilever image width ~100 micrometers. b) ~30 micrometers

If the tip was scanned at a constant height, a risk would exist that the tip collides with the surface, causing damage. Hence, in most cases a feedback mechanism is employed to adjust the tip-to-sample distance to maintain a constant force between the tip and the sample. Traditionally, the sample is mounted on a piezoelectric tube that can move the sample in the z direction for maintaining a constant force, and the x and y directions for scanning the sample. Alternatively a 'tripod' configuration of three piezo crystals may be employed, with each responsible for scanning in the x,y and z directions. This eliminates some of the distortion effects seen with a tube scanner. In newer designs, the tip is mounted on a vertical piezo scanner while the sample is being scanned in X and Y using another piezo block. The resulting map of the area z = f(x, y) represents the topography of the sample.

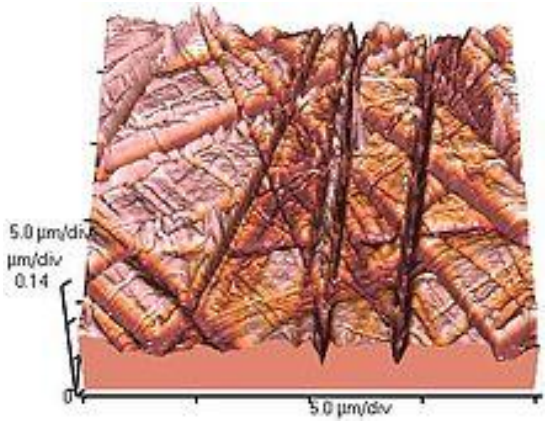


Figure-1.23.Atomic force microscope topographical scan of a glass surface. The micro and nano-scale features of the glass can be observed, portraying the roughness of the material. The image space is (x,y,z) = (20 µm × 20 µm × 420 nm).

The AFM can be operated in a number of modes, depending on the application. In general, possible imaging modes are divided into static (also called contact) modes and a variety of dynamic (or non-contact) modes where the cantilever is vibrated.

Imaging modes

The primary modes of operation for an AFM are static mode and dynamic mode. In static mode, the cantilever is "dragged" across the surface of the sample and the contours of the surface are measured directly using the deflection of the cantilever. In the dynamic mode, the

cantilever is externally oscillated at or close to its fundamental resonance frequency or a harmonic. The oscillation amplitude, phase and resonance frequency are modified by tip-sample interaction forces. These changes in oscillation with respect to the external reference oscillation provide information about the sample's characteristics.

Contact mode

In the static mode operation, the static tip deflection is used as a feedback signal. Because the measurement of a static signal is prone to noise and drift, low stiffness cantilevers are used to boost the deflection signal. However, close to the surface of the sample, attractive forces can be quite strong, causing the tip to "snap-in" to the surface. Thus static mode AFM is almost always done in contact where the overall force is repulsive. Consequently, this technique is typically called "contact mode". In contact mode, the force between the tip and the surface is kept constant during scanning by maintaining a constant deflection.

Non-contact mode

In this mode, the tip of the cantilever does not contact the sample surface. The cantilever is instead oscillated at a frequency slightly above its resonant frequency where the amplitude of oscillation is typically a few nanometres (<10 nm).

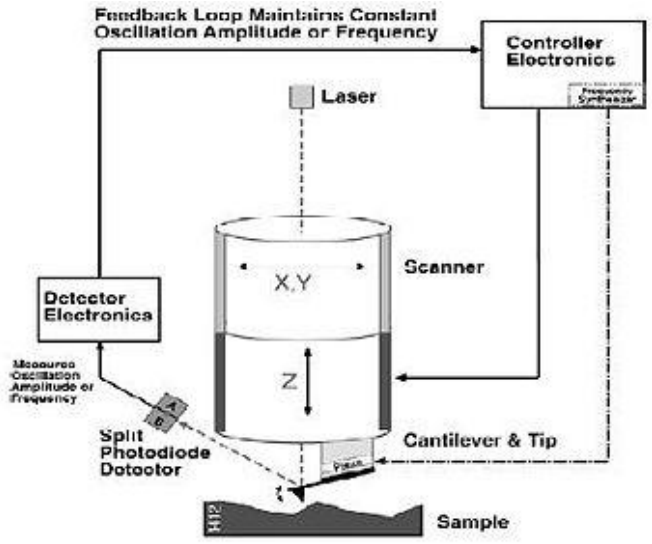


Figure-1.24.AFM – non-contact mode

The van der Waals forces, which are strongest from 1 nm to 10 nm above the surface, or any other long range force which extends above the surface acts to decrease the resonance frequency of the cantilever This decrease in resonant frequency combined with the feedback loop system maintains a constant oscillation amplitude or frequency by adjusting the average tip-to-sample distance. Measuring the tip-to-sample distance at each (x,y) data point allows the scanning software to construct a topographic image of the sample surface. Non-contact mode AFM does not suffer from tip or sample degradation effects that are sometimes observed after taking numerous scans with contact AFM. This makes non-contact AFM preferable to contact AFM for measuring soft samples. In the case of rigid samples, contact and non-contact images may look the same. However, if a few monolayers of adsorbed fluid

are lying on the surface of a rigid sample, the images may look quite different. An AFM operating in contact mode will penetrate the liquid layer to image the underlying surface, whereas in non-contact mode an AFM will oscillate above the adsorbed fluid layer to image both the liquid and surface. Schemes for dynamic mode operation include frequency modulation and the more common amplitude modulation. In frequency modulation, changes in the oscillation frequency provide information about tip-sample interactions. Frequency can be measured with very high sensitivity and thus the frequency modulation mode allows for the use of very stiff cantilevers. Stiff cantilevers provide stability very close to the surface and, as a result, this technique was the first AFM technique to provide true atomic resolution in ultra-high vacuum conditions.

In amplitude modulation, changes in the oscillation amplitude or phase provide the feedback signal for imaging. In amplitude modulation, changes in the phase of oscillation can be used to discriminate between different types of materials on the surface. Amplitude modulation can be operated either in the non-contact or in the intermittent contact regime. In dynamic contact mode, the cantilever is oscillated such that the separation distance between the cantilever tip and the sample surface is modulated. Amplitude modulation has also been used in the non-contact regime to image with atomic resolution by using very stiff cantilevers and small amplitudes in an ultra-high vacuum environment.

Tapping mode

In ambient conditions, most samples develop a liquid meniscus layer. Because of this, keeping the probe tip close enough to the sample for short-range forces to become detectable while preventing the tip from sticking to the surface presents a major problem for non-contact dynamic mode in ambient conditions. Dynamic contact mode (also called intermittent contact or tapping mode) was developed to bypass this problem.. In tapping mode, also called "AC Mode" or "intermittent contact mode", the cantilever is driven to oscillate up and down at near its resonance frequency by a small piezoelectric element mounted in the AFM tip holder similar to non-contact mode. However, the amplitude of this oscillation is greater than 10 nm, typically 100 to 200 nm. Due to the interaction of forces acting on the cantilever when the tip comes close to the surface, Van der Waals force, dipole-dipole interaction, electrostatic forces, etc. cause the amplitude of this oscillation to decrease as the tip gets closer to the sample. An electronic servo uses the piezoelectric actuator to control the height of the cantilever above the sample. The servo adjusts the height to maintain a set cantilever oscillation amplitude as the cantilever is scanned over the sample.

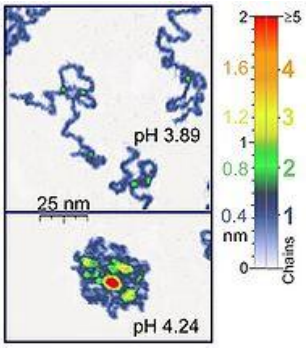


Figure-1.25.Single polymer chains (0.4 nm thick) recorded in a tapping mode under aqueous media with different pH

A tapping AFM image is therefore produced by imaging the force of the intermittent contacts of the tip with the sample surface.

This method of "tapping" lessens the damage done to the surface and the tip compared to the amount done in contact mode. Tapping mode is gentle enough even for the visualization of supported lipid bilayers or adsorbed single polymer molecules (for instance, 0.4 nm thick chains of synthetic polyelectrolytes) under liquid medium. With proper scanning parameters, the conformation of single molecules can remain unchanged for hours.[2]

AFM cantilever deflection measurement

AFM beam deflection detection

Laser light from a solid state diode is reflected off the back of the cantilever and collected by a position sensitive detector (PSD) consisting of two closely spaced photodiodes whose output signal is collected by a differential amplifier

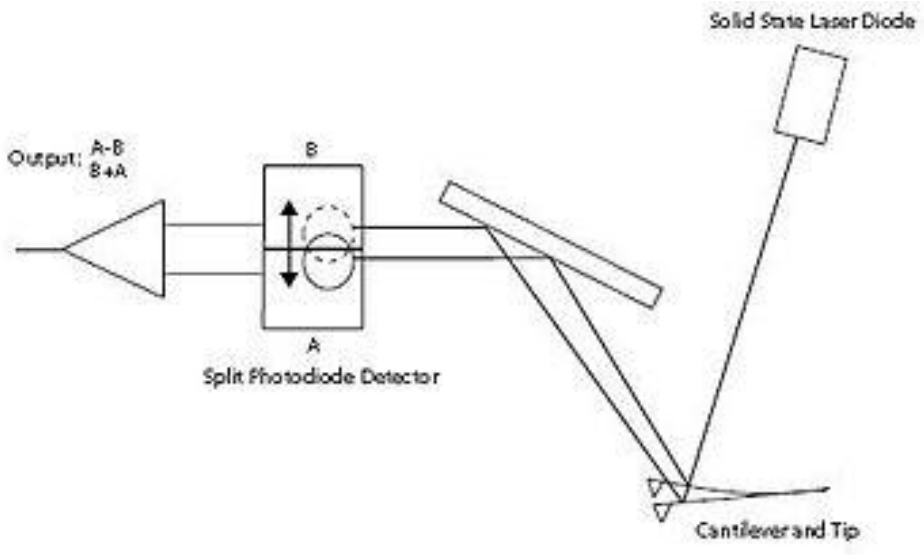


Figure-1.26.AFM cantilever deflection measurement

Angular displacement of the cantilever results in one photodiode collecting more light than the other photodiode, producing an output signal (the difference between the photodiode signals normalized by their sum) which is proportional to the deflection of the cantilever. It detects cantilever deflections <10 nm (thermal noise limited). A long beam path (several centimeters) amplifies changes in beam angle.

Applications of AFM

1. Force spectroscopy

Another major application of AFM (besides imaging) is force spectroscopy, the direct measurement of tip-sample interaction forces as a function of the gap between the tip and sample (the result of this measurement is called a force-distance curve). For this method, the AFM tip is extended towards and retracted from the surface as the deflection of the cantilever

is monitored as a function of piezoelectric displacement. These measurements have been used to measure nanoscale contacts, atomic bonding, Van der Waals forces, and Casimir forces, dissolution forces in liquids and single molecule stretching and rupture forces.[5] Furthermore, AFM was used to measure, in an aqueous environment, the dispersion force due to polymer adsorbed on the substrate. Forces of the order of a few piconewtons can now be routinely measured with a vertical distance resolution of better than 0.1 nanometers. Force spectroscopy can be performed with either static or dynamic modes. In dynamic modes, information about the cantilever vibration is monitored in addition to the static deflection.

Problems with the technique include no direct measurement of the tip-sample separation and the common need for low stiffness cantilevers which tend to 'snap' to the surface. The snap-in can be reduced by measuring in liquids or by using stiffer cantilevers, but in the latter case a more sensitive deflection sensor is needed. By applying a small dither to the tip, the stiffness (force gradient) of the bond can be measured as well.

2. Identification of individual surface atoms

The AFM can be used to image and manipulate atoms and structures on a variety of surfaces. The atom at the apex of the tip "senses" individual atoms on the underlying surface when it forms incipient chemical bonds with each atom. Because these chemical interactions subtly alter the tip's vibration frequency, they can be detected and mapped. This principle was used to distinguish between atoms of silicon, tin and lead on an alloy surface, by comparing these 'atomic fingerprints' to values obtained from large-scale density functional theory (DFT) simulations.

The trick is to first measure these forces precisely for each type of atom expected in the sample, and then to compare with forces given by DFT simulations. The team found that the tip interacted most strongly with silicon atoms, and interacted 23% and 41% less strongly with tin and lead atoms, respectively. Thus, each different type of atom can be identified in the matrix as the tip is moved across the surface.

Advantages and disadvantages

Just like any other tool, an AFM's usefulness has limitations. When determining whether or not analyzing a sample with an AFM is appropriate, there are various advantages and disadvantages that must be considered.

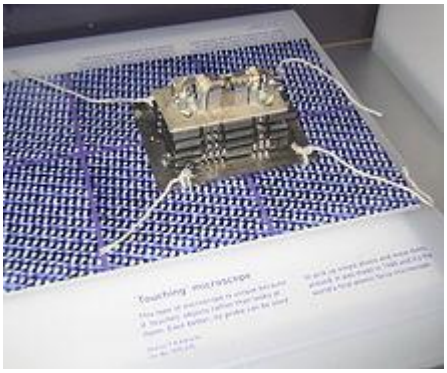


Figure-1.27.The first atomic force microscope

Advantages

AFM has several advantages over the scanning electron microscope (SEM). Unlike the electron microscope which provides a two-dimensional projection or a two-dimensional image of a sample, the AFM provides a three-dimensional surface profile. Additionally, samples viewed by AFM do not require any special treatments (such as metal/carbon coatings) that would irreversibly change or damage the sample, and does not typically suffer from charging artifacts in the final image. While an electron microscope needs an expensive vacuum environment for proper operation, most AFM modes can work perfectly well in ambient air or even a liquid environment. This makes it possible to study biological macromolecules and even living organisms. In principle, AFM can provide higher resolution than SEM. It has been shown to give true atomic resolution in ultra-high vacuum (UHV) and, more recently, in liquid environments. High resolution AFM is comparable in resolution to scanning tunneling microscopy and transmission electron microscopy. AFM can also be combined with a variety of optical microscopy techniques, further expanding its applicability. Combined AFM-optical instruments have been applied primarily in the biological sciences but has also found a niche in some materials applications, especially those involving photovoltaics research .

Disadvantages

A disadvantage of AFM compared with the scanning electron microscope (SEM) is the single scan image size. In one pass, the SEM can image an area on the order of square millimeters with a depth of field on the order of millimeters, whereas the AFM can only image a maximum height on the order of 10-20 micrometers and a maximum scanning area of about 150×150 micrometers. One method of improving the scanned area size for AFM is by using parallel probes in a fashion similar to that of millipede data storage.

The scanning speed of an AFM is also a limitation. Traditionally, an AFM cannot scan images as fast as a SEM, requiring several minutes for a typical scan, while a SEM is capable of scanning at near real-time, although at relatively low quality. The relatively slow rate of scanning during AFM imaging often leads to thermal drift in the image making the AFM microscope less suited for measuring accurate distances between topographical features on the image. However, several fast-acting designs were suggested to increase microscope scanning productivity including what is being termed video AFM (reasonable quality images are being obtained with video AFM at video rate: faster than the average SEM). To eliminate image distortions induced by thermal drift, several methods have been introduced.

AFM images can also be affected by nonlinearity, hysteresis, and creep of the piezoelectric material and cross-talk between the x, y, z axes that may require software enhancement and filtering. Such filtering could "flatten" out real topographical features. However, newer AFMs utilize real-time correction software (for example, feature-oriented scanning) or closed-loop scanners which practically eliminate these problems. Some AFMs also use separated orthogonal scanners (as opposed to a single tube) which also serve to eliminate part of the cross-talk problems.

As with any other imaging technique, there is the possibility of image artifacts, which could be induced by an unsuitable tip, a poor operating environment, or even by the sample itself. These image artifacts are unavoidable however, their occurrence and effect on results can be reduced through various methods.

Due to the nature of AFM probes, they cannot normally measure steep walls or overhangs. Specially made cantilevers and AFMs can be used to modulate the probe sideways as well as up and down (as with dynamic contact and non-contact modes) to measure sidewalls, at the cost of more expensive cantilevers, lower lateral resolution and additional artifacts.

1.8.2.1.5. Scanning Tunnelling Microscope

A scanning tunnelling microscope (STM) is an instrument for imaging surfaces at the atomic level. Its development in 1981 earned its inventors, Gerd Binnig and Heinrich Rohrer (at IBM Zürich), the Nobel Prize in Physics in 1986. For an STM, good resolution is considered to be 0.1 nm lateral resolution and 0.01 nm depth resolution. With this resolution, individual atoms within materials are routinely imaged and manipulated. The STM can be used not only in ultra-high vacuum but also in air, water, and various other liquid or gas ambients, and at temperatures ranging from near zero kelvin to a few hundred degrees Celsius.

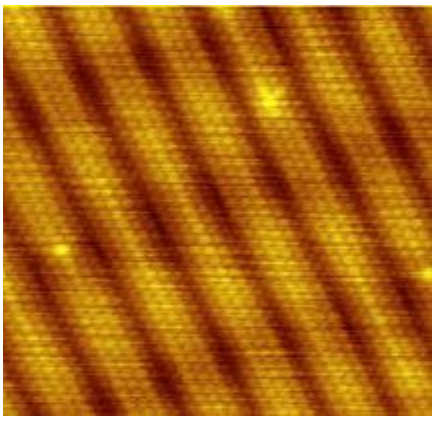


Figure-1.28.Image of reconstruction on a clean Gold (100) surface

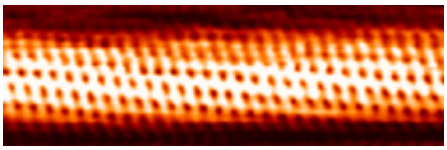


Figure-1.29.An STM image of a single-walled carbon nanotube

The STM is based on the concept of quantum tunnelling. When a conducting tip is brought very near to the surface to be examined, a bias (voltage difference) applied between the two can allow electrons to tunnel through the vacuum between them. The resulting tunneling current is a function of tip position, applied voltage, and the local density of states (LDOS) of the sample. Information is acquired by monitoring the current as the tip's position scans across the surface, and is usually displayed in image form. STM can be a challenging technique, as it requires extremely clean and stable surfaces, sharp tips, excellent vibration control, and sophisticated electronics.

Instrumentation

The components of an STM include scanning tip, piezoelectric controlled height and x,y scanner, coarse sample-to-tip control, vibration isolation system, and computer

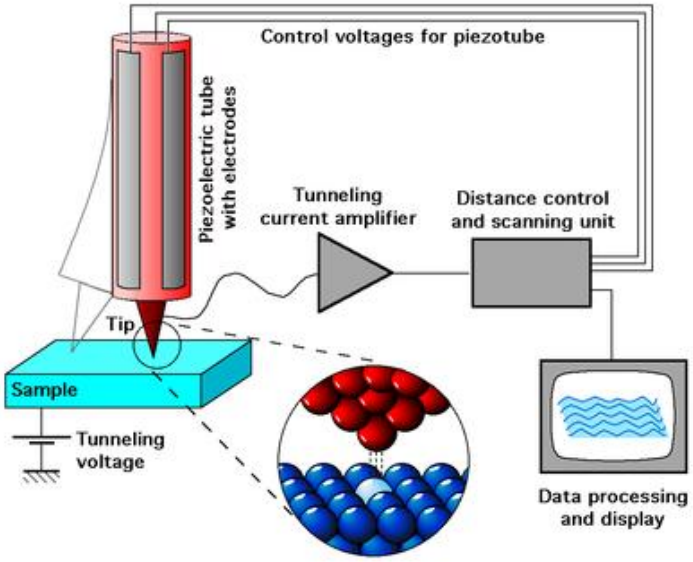


Figure-1.30.Schematic view of an STM

The resolution of an image is limited by the radius of curvature of the scanning tip of the STM.Additionally,image artifacts can occur if the tip has two tips at the end rather than a single atom; this leads to "double-tip imaging," a situation in which both tips contribute to the tunneling. Therefore it has been essential to develop processes for consistently obtaining sharp, usable tips. Recently, carbon nanotubes have been used in this instance.

The tip is often made of tungsten or platinum-iridium, though gold is also used. Tungsten tips are usually made by electrochemical etching, and platinum-iridium tips by mechanical shearing. Due to the extreme sensitivity of tunnel current to height, proper vibration isolation or an extremely rigid STM body is imperative for obtaining usable results. In the first STM by Binnig and Rohrer, magnetic levitation was used to keep the STM free from vibrations; now mechanical spring or gas spring systems are often used. Additionally, mechanisms for reducing eddy currents are sometimes implemented. Maintaining the tip position with respect to the sample, scanning the sample and acquiring the data is computer controlled. The computer may also be used for enhancing the image with the help of image processing as well as performing quantitative measurements.

Many other microscopy techniques have been developed based upon STM. These include photon scanning microscopy (PSTM), which uses an optical tip to tunnel photons; scanning tunneling potentiometry (STP), which measures electric potential across a surface; spin polarized scanning tunneling microscopy (SPSTM), which uses a ferromagnetic tip to tunnel spin-polarized electrons into a magnetic sample, and atomic force microscopy (AFM), in which the force caused by interaction between the tip and sample is measured.

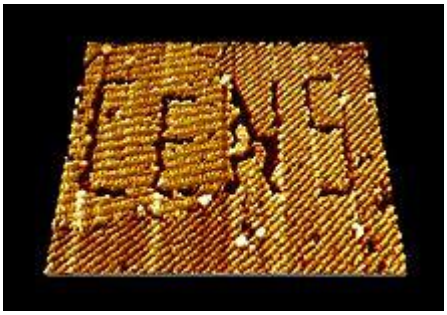


Figure-1.31.Nanomanipulation via STM of a self-assembled organic semiconductor monolayer (here: PTCDA molecules) on graphite, in which the logo of the Center for NanoScience (CeNS), LMU has been written.

Other STM methods involve manipulating the tip in order to change the topography of the sample. This is attractive for several reasons. Firstly the STM has an atomically precise positioning system which allows very accurate atomic scale manipulation. Furthermore, after the surface is modified by the tip, it is a simple matter to then image with the same tip, without changing the instrument. IBM researchers developed a way to manipulate Xenon atoms adsorbed on a nickel surface. This technique has been used to create electron "corrals" with a small number of adsorbed atoms, which allows the STM to be used to observe electron Friedel oscillations on the surface of the material. Aside from modifying the actual sample surface, one can also use the STM to tunnel electrons into a layer of E-Beam photoresist on a sample, in order to do lithography. This has the advantage of offering more control of the exposure than traditional Electron beam lithography. Another practical application of STM is atomic deposition of metals (Au, Ag, W, etc.) with any desired (pre-programmed) pattern, which can be used as contacts to nanodevices or as nanodevices themselves.

Working

First, a voltage bias is applied and the tip is brought close to the sample by some coarse sample-to-tip control, which is turned off when the tip and sample are sufficiently close. At close range, fine control of the tip in all three dimensions when near the sample is typically piezoelectric, maintaining tip-sample separation W typically in the 4-7 Å range, which is the equilibrium position between attractive (3<W<10Å) and repulsive (W<3Å) interactions. In this situation, the voltage bias will cause electrons to tunnel between the tip and sample, creating a current that can be measured. Once tunneling is established, the tip's bias and position with respect to the sample can be varied (with the details of this variation depending on the experiment) and data are obtained from the resulting changes in current.During operation of an STM the tip is brought close to the surface under coarse control and then to an equilibrium position between tip attraction and repulsion which is typically within a range from 4 to 7Å. When the conducting tip is brought so close to the surface, a bias between the two can allow electrons to tunnel between them. At low voltages, this current provides a record to the surface height. For tunnelling to take place, both the sample and the tip must be conductors or semiconductors. Unlike AFMs, STMs in principle cannot image insulating materials. However if a tunnelling current can be produced from a water layer, then the insulating material can be seen. This is particularly important for biological materials. If the tip is moved across the sample in the x-y plane, the changes in surface height and density of states cause changes in current. These changes are mapped in images. This change in current with respect to position can be measured itself, or the height, z, of the tip corresponding to a

constant current can be measured. These two modes are called constant height mode and constant current mode, respectively.

Much of the other operations are like AFMs

In constant height mode the tip travels in a horizontal plane above the sample and the tunnelling current varies depending on topography and the local surface electronic properties of the sample. Similarly, the tunnelling current measured at each location on the sample surface constitutes the topographic image. In constant height mode, the voltage and height are both held constant while the current changes to keep the voltage from changing; this leads to an image made of current changes over the surface, which can be related to charge density. The benefit to using a constant height mode is that it is faster, as the piezoelectric movements require more time to register the height change in constant current mode, than the voltage change in constant height mode. All images produced by STM are grayscale, with color optionally added in post-processing in order to visually emphasize important features.

In constant current mode STMs use feedback to keep the tunnelling current constant by adjusting the height of the scanner at each measurement point. For example, when the system detects an increase in tunnelling current, it adjusts the voltage applied to the scanner to increase the distance between the tip and the sample. In constant current mode, feedback electronics adjust the height by a voltage to the piezoelectric height control mechanism. This leads to a height variation and thus the image comes from the tip topography across the sample and gives a constant charge density surface; this means contrast on the image is due to variations in charge density. In constant-current mode, the motion of the scanner constitutes the data set. If the system keeps the tunnelling current constant to within a few percent, the tip-to-sample distance will be constant within a few tenths of a nanometre. The change in voltage necessary to keep this constant distance is of course also a measure of topography, but it can mean other things.

Each mode has advantages and disadvantages.

Constant height mode is faster because the system doesn't have to move the scanner up and down, but it provides useful information only for relatively smooth surfaces.

Constant-current mode can measure irregular surfaces with height precision, but the measurement takes more time.

Applications

More accurately, the tunnelling current corresponds to the electronic density of states at the surface. STMs actually sense the number of filed or unfilled electron states near the surface, within an energy range determined by the bias voltage. Rather than really measuring physical topography, it measures a surface of constant tunnelling probability. The sensitivity of STMs to local electronic structure can cause misinterpretation. For example, if an area if the sample has oxidized, that is, has lost electrons, the tunnelling current will drop precipitously when the tip encounters that area. In constant-current mode, the STM will instruct the tip to move closer to maintain the set tunnelling current. The result may be that the tip digs a hole in the

surface. Nevertheless, the sensitivity of STMs to electronic structure can be a tremendous advantage in some studies since it can tell us about electron deficient sites or electron-rich mines.

Both AFM and STM can be used in systems that have adsorbed molecules, such as water. The response is often different to that without a water layer because the water layer exerts a capillary force that is very strong and attractive. As the scanner pulls away from the surface, the water holds the tip in contact with the surface, bending the cantilever strongly towards the surface. At some point, depending upon the thickness of the water layer, the scanner retracts enough so that the tip springs free. This is known as the snap-back point. Snap-back point varies with adsorbent; and the positions and amplitudes of the snap-back points depend upon the viscosity and thickness of the layers present on the surface.

Liquid cells for the STM allow operation with the tip and the sample fully submerged in liquid, providing the capability for imaging hydrated samples. When imaging in solution a further control is afforded samples when imaging in solution a further control is afforded by the choice of solution, since is some solutions there is a double layer of ions on the surface that can be studied or moved. A liquid environment is useful for a variety of STM applications, including studies of biology, geologic systems, corrosion, or any surface study where a solid-liquid interface is involved. Electrochemical cells (EC) also provide a controlled environment for STM operation. Applications of EC-STM include real-space imaging of electronic and structural properties of electrodes, including changes induced by chemical and electrochemical processes, phase formation, adsorption, and corrosion, as well as deposition of organic and biological molecules in electrolytic solution

Figure-1.32.A close-up of a simple scanning tunnelling microscope head using a platinum-iridium tip.

In addition to scanning across the sample, information on the electronic structure at a given location in the sample can be obtained by sweeping voltage and measuring current at a specific location. This type of measurement is called scanning tunneling spectroscopy (STS) and typically results in a plot of the local density of states as a function of energy within the sample. The advantage of STM over other measurements of the density of states lies in its ability to make extremely local measurements: for example, the density of states at an impurity site can be compared to the density of states far from impurities. Framerates of at

least 1 Hz enable so called Video-STM (up to 50 Hz is possible). This can be used to scan surface diffusion.

1.8.2.2. Lithographic Techniques used to "Measure the Internal Geometries of Nanostructures"

1.8.2.2.1. 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.

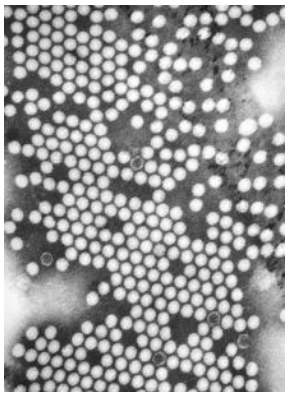


Figure-1.33.A TEM image of the polio virus. The polio virus is 30 nm in size

TEMs are capable of imaging at a significantly higher resolution than light microscopes, owing to the small de Broglie wavelength of electrons. This enables the instrument's user to examine fine detail—even as small as a single column of atoms, which is tens of thousands times smaller than the smallest resolvable object in a light microscope. TEM forms a major analysis method in a range of scientific fields, in both physical and biological sciences. TEMs find application in cancer research, virology, materials science as well as pollution, nanotechnology, and semiconductor research. At smaller magnifications TEM image contrast is due to absorption of electrons in the material, due to the thickness and composition of the material. At higher magnifications complex wave interactions modulate the intensity of the image, requiring expert analysis of observed images. Alternate modes of use allow for the TEM to observe modulations in chemical identity, crystal orientation, electronic structure and sample induced electron phase shift as well as the regular absorption based imaging. The first TEM was built by Max Knoll and Ernst Ruska in 1931, with this group developing the first TEM with resolving power greater than that of light in 1933 and the first commercial TEM in 1939.

History:-Initial development

Ernst Abbe originally proposed that the ability to resolve detail in an object was limited by the wavelength of the light used in imaging, thus limiting the useful obtainable magnification from an optical microscope to a few micrometers. Developments into ultraviolet (UV) microscopes, led by Köhler and Rohr, allowed for an increase in resolving power of about a factor of two. However this required more expensive quartz optical components, due to the absorption of UV by glass. At this point it was believed that obtaining an image with sub-micrometer information was simply impossible due to this wavelength constraint.

Figure-1.34.The first practical TEM, Originally installed at I. G Farben-Werke and now on display at the Deutsches Museum in Munich, Germany

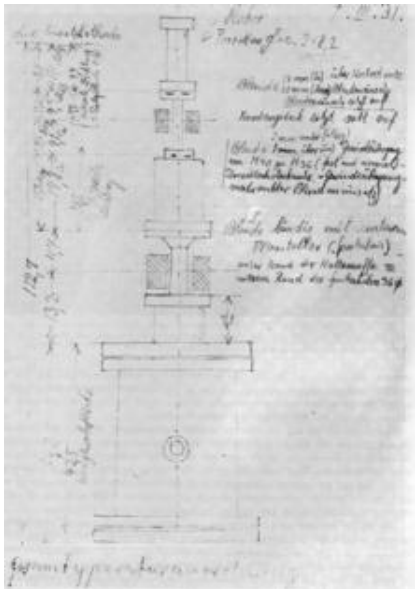


Figure-1.35.Sketch of first electron microscope, originally from Ruska's notebook in 1931, capable of only 16 times magnification

It had earlier been recognized by Plücker in 1858 that the deflection of "cathode rays" (electrons) was possible by the use of magnetic fields. This effect had been utilised to build primitive cathode ray oscilloscopes (CROs) as early as 1897 by Ferdinand Braun, intended as a measurement device. Indeed in 1891 it was recognized by Riecke that the cathode rays could be focused by these magnetic fields, allowing for simple lens designs. Later this theory was extended by Hans Busch in his work published in 1926, who showed that the lens maker's equation, could under appropriate assumptions, be applicable to electrons.

In 1928, at the Technological University of Berlin Adolf Matthias, Professor of High voltage Technology and Electrical Installations, appointed Max Knoll to lead a team of researchers to advance the CRO design. The team consisted of several PhD students including Ernst Ruska and Bodo von Borries. This team of researchers concerned themselves with lens design and CRO column placement, which they attempted to obtain the parameters that could be optimised to allow for construction of better CROs, as well as the development of electron optical components which could be used to generate low magnification (nearly 1:1) images. In 1931 the group successfully generated magnified images of mesh grids placed over the anode aperture. The device used two magnetic lenses to achieve higher magnifications, arguably the first electron microscope. In that same year, Reinhold Rudenberg, the scientific director of the Siemens company, had patented an electrostatic lens electron microscope.

Improving resolution

At this time the wave nature of electrons, which were considered charged matter particles, had not been fully realised until the publication of the De Broglie hypothesis in 1927. The group was unaware of this publication until 1932, where it was quickly realized that the De Broglie wavelength of electrons was many orders of magnitude smaller than that for light, theoretically allowing for imaging at atomic scales. In April 1932, Ruska suggested the construction of a new electron microscope for direct imaging of specimens inserted into the microscope, rather than simple mesh grids or images of apertures. With this device successful diffraction and normal imaging of aluminium sheet was achieved, however exceeding the magnification achievable with light microscopy had still not been successfully demonstrated. This goal was achieved in September 1933, using images of cotton fibers, which were quickly acquired before being damaged by the electron beam.

At this time, interest in the electron microscope had increased, with other groups, such as Albert Prebus and James Hillier at the University of Toronto who constructed the first TEM in North America in 1938, continually advancing TEM design.

Research continued on the electron microscope at Siemens in 1936, the aim of the research was the development improvement of TEM imaging properties, particularly with regard to biological specimens. At this time electron microscopes were being fabricated for specific groups, such as the "EM1" device used at the UK National Physical Laboratory. In 1939 the first commercial electron microscope, pictured, was installed in the Physics department of I. G Farben-Werke. Further work on the electron microscope was hampered by the destruction of a new laboratory constructed at Siemens by an air-raid, as well as the death of two of the researchers, Heinz Müller and Friedrick Krause during World War II.

Further research

After World War II, Ruska resumed work at Siemens, where he continued to develop the electron microscope, producing the first microscope with 100k magnification. The fundamental structure of this microscope design, with multi-stage beam preparation optics, is still used in modern microscopes. The worldwide electron microscopy community advanced with electron microscopes being manufactured in Manchester UK, the USA (RCA), Germany (Siemens) and Japan . The first international conference in electron microscopy was in Delft in 1942, with more than one hundred attendees. Later conferences included the "First" international conference in Paris, 1950 and then in London in 1954.

With the development of TEM, the associated technique of scanning transmission electron microscopy (STEM) was re-investigated and did not become developed until the 1970s, with Albert Crewe at the University of Chicago developing the field emission gun and adding a high quality objective lens to create the modern STEM. Using this design, Crewe demonstrated the ability to image atoms using annular dark-field imaging. Crewe and co-workers at the University of Chicago developed the cold field electron emission source and built a STEM able to visualize single heavy atoms on thin carbon substrates.

Background

Electrons

Theoretically, the maximum resolution, d, that one can obtain with a light microscope has been limited by the wavelength of the photons that are being used to probe the sample, λ and the numerical aperture of the system, NA.

$$d = \frac{\lambda}{2n\sin\alpha} \approx \frac{\lambda}{2\,\mathrm{NA}}$$

Early twentieth century scientists theorised ways of getting around the limitations of the relatively large wavelength of visible light (wavelengths of 400–700 nanometers) by using electrons. Like all matter, electrons have both wave and particle properties (as theorized by Louis-Victor de Broglie), and their wave-like properties mean that a beam of electrons can be made to behave like a beam of electromagnetic radiation. The wavelength of electrons is found by equating the de Broglie equation to the kinetic energy of an electron. An additional correction must be made to account for relativistic effects, as in a TEM an electron's velocity approaches the speed of light, c.

$$\lambda_e \approx \frac{h}{\sqrt{2m_0E\left(1+\frac{E}{2m_0c^2}\right)}}$$

where, h is Planck's constant, m_0 is the rest mass of an electron and E is the energy of the accelerated electron. Electrons are usually generated in an electron microscope by a process known as thermionic emission from a filament, usually tungsten, in the same manner as a light bulb, or alternatively by field electron emission. The electrons are then accelerated by an electric potential (measured in volts) and focused by electrostatic and electromagnetic lenses

onto the sample. The transmitted beam contains information about electron density, phase and periodicity; this beam is used to form an image.

Source formation

From the top down, the TEM consists of an emission source, which may be a tungsten filament, or a lanthanum hexaboride (LaB_6) source. For tungsten, this will be of the form of either a hairpin-style filament, or a small spike-shaped filament.

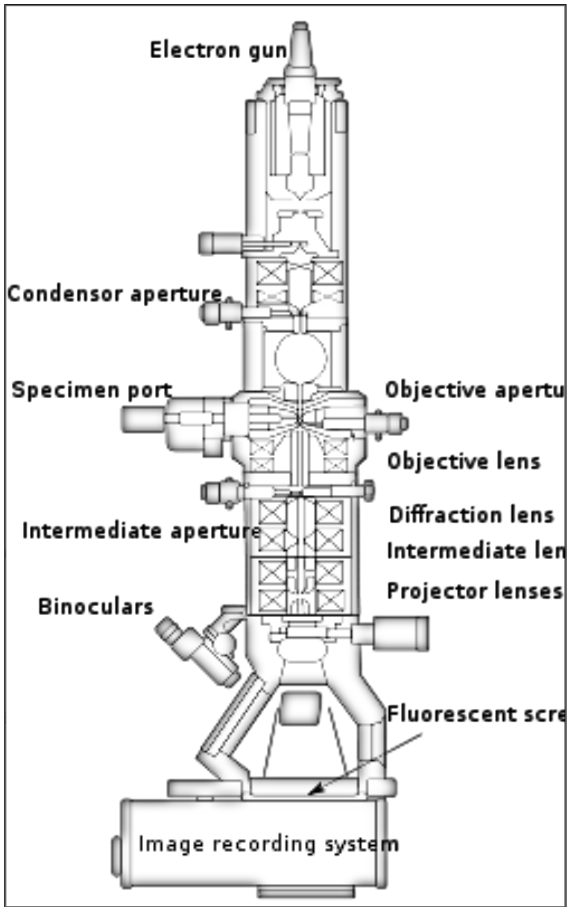


Figure-1.36.Layout of optical components in a basic TEM

LaB_6 sources utilize small single crystals. By connecting this gun to a high voltage source (typically ~100-300 kV) the gun will, given sufficient current, begin to emit electrons either by thermionic or field electron emission into the vacuum. This extraction is usually aided by the use of a Wehnelt cylinder. Once extracted, the upper lenses of the TEM allow for the formation of the electron probe to the desired size and location for later interaction with the sample.

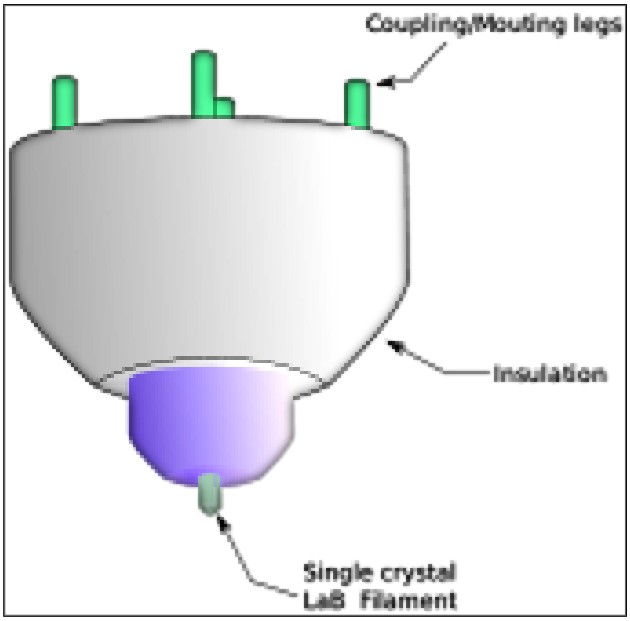


Figure-1.37.Single crystal LaB_6 filament

Manipulation of the electron beam is performed using two physical effects.

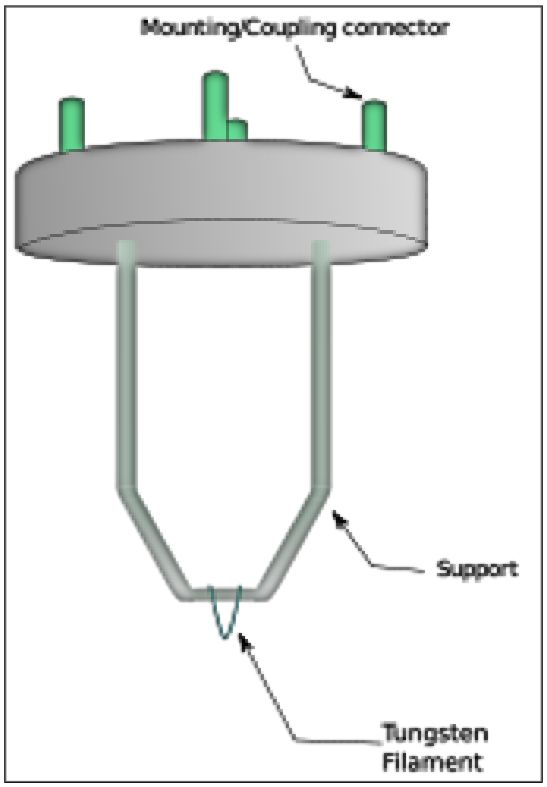


Figure-1.38.Hairpin style tungsten filament

The interaction of electrons with a magnetic field will cause electrons to move according to the right hand rule, thus allowing for electromagnets to manipulate the electron beam. The use of magnetic fields allows for the formation of a magnetic lens of variable focusing power,

the lens shape originating due to the distribution of magnetic flux. Additionally, electrostatic fields can cause the electrons to be deflected through a constant angle.

Coupling of two deflections in opposing directions with a small intermediate gap allows for the formation of a shift in the beam path, this being used in TEM for beam shifting, subsequently this is extremely important to STEM. From these two effects, as well as the use of an electron imaging system, sufficient control over the beam path is possible for TEM operation. The optical configuration of a TEM can be rapidly changed, unlike that for an optical microscope, as lenses in the beam path can be enabled, have their strength changed, or be disabled entirely simply via rapid electrical switching, the speed of which is limited by effects such as the magnetic hysteresis of the lenses.

Optics

The lenses of a TEM allow for beam convergence, with the angle of convergence as a variable parameter, giving the TEM the ability to change magnification simply by modifying the amount of current that flows through the coil, quadrupole or hexapole lenses. The quadrupole lens is an arrangement of electromagnetic coils at the vertices of the square, enabling the generation of a lensing magnetic fields, the hexapole configuration simply enhances the lens symmetry by using six, rather than four coils.

Typically a TEM consists of three stages of lensing. The stages are the condensor lenses, the objective lenses, and the projector lenses. The condensor lenses are responsible for primary beam formation, whilst the objective lenses focus the beam that comes through the sample itself (in STEM scanning mode, there are also objective lenses above the sample to make the incident electron beam convergent). The projector lenses are used to expand the beam onto the phosphor screen or other imaging device, such as film. The magnification of the TEM is due to the ratio of the distances between the specimen and the objective lens' image plane. Additional quad or hexapole lenses allow for the correction of asymmetrical beam distortions, known as astigmatism. It is noted that TEM optical configurations differ significantly with implementation, with manufacturers using custom lens configurations, such as in spherical aberration corrected instruments, or TEMs utilising energy filtering to correct electron chromatic aberration.

Display

Imaging systems in a TEM consist of a phosphor screen, which may be made of fine (10-100 μm) particulate zinc sulphide, for direct observation by the operator. Optionally, an image recording system such as film based or doped YAG screen coupled CCDs. Typically these devices can be removed or inserted into the beam path by the operator as required.

Components

A TEM is composed of several components, which include a vacuum system in which the electrons travel, an electron emission source for generation of the electron stream, a series of electromagnetic lenses, as well as electrostatic plates.

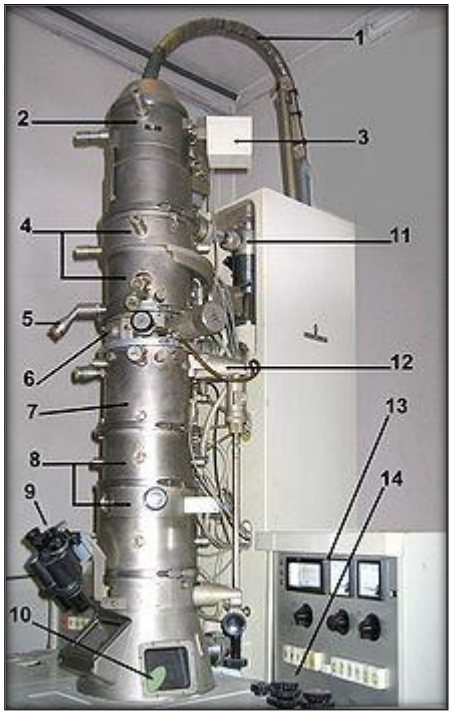


Figure-1.39.The electron source of the TEM is at the top, where the lensing system (4,7 and 8) focuses the beam on the specimen and then projects it onto the viewing screen (10). The beam control is on the right (13 and 14)

The latter two allow the operator to guide and manipulate the beam as required. Also required is a device to allow the insertion into, motion within, and removal of specimens from the beam path. Imaging devices are subsequently used to create an image from the electrons that exit the system.

Vacuum system

To increase the mean free path of the electron gas interaction, a standard TEM is evacuated to low pressures, typically on the order of 10^{-4} Pa. The need for this is twofold: first the allowance for the voltage difference between the cathode and the ground without generating an arc, and secondly to reduce the collision frequency of electrons with gas atoms to negligible levels—this effect is characterised by the mean free path. TEM components such as specimen holders and film cartridges must be routinely inserted or replaced requiring a system with the ability to re-evacuate on a regular basis. As such, TEMs are equipped with multiple pumping systems and airlocks and are not permanently vacuum sealed.

The vacuum system for evacuating a TEM to an operating pressure level consists of several stages. Initially a low or roughing vacuum is achieved with either a rotary vane pump or diaphragm pumps bringing the TEM to a sufficiently low pressure to allow the operation of a turbomolecular or diffusion pump which brings the TEM to its high vacuum level necessary for operations. To allow for the low vacuum pump to not require continuous operation, while continually operating the turbomolecular pumps, the vacuum side of a low-pressure pump may be connected to chambers which accommodate the exhaust gases from the turbomolecular pump. Sections of the TEM may be isolated by the use of gate valves, to allow for different vacuum levels in specific areas, such as a higher vacuum of 10^{-4} to 10^{-7} Pa or higher in the electron gun in high-resolution or field-emission TEMs.

High-voltage TEMs require ultra-high vacuums on the range of 10^{-7} to 10^{-9} Pa to prevent generation of an electrical arc, particularly at the TEM cathode. As such for higher voltage TEMs a third vacuum system may operate, with the gun isolated from the main chamber either by use of gate valves or by the use of a differential pumping aperture. The differential pumping aperture is a small hole that prevents diffusion of gas molecules into the higher vacuum gun area faster than they can be pumped out. For these very low pressures either an ion pump or a getter material is used.

Poor vacuum in a TEM can cause several problems, from deposition of gas inside the TEM onto the specimen as it is being viewed through a process known as electron beam induced deposition, or in more severe cases damage to the cathode from an electrical discharge. Vacuum problems due to specimen sublimation are limited by the use of a cold trap to adsorb sublimated gases in the vicinity of the specimen.

Specimen stage

TEM specimen stage designs include airlocks to allow for insertion of the specimen holder into the vacuum with minimal increase in pressure in other areas of the microscope. The specimen holders are adapted to hold a standard size of grid upon which the sample is placed or a standard size of self-supporting specimen. Standard TEM grid sizes is a 3.05 mm diameter ring, with a thickness and mesh size ranging from a few to 100 μm. The sample is placed onto the inner meshed area having diameter of approximately 2.5 mm. Usual grid materials are copper, molybdenum, gold or platinum.

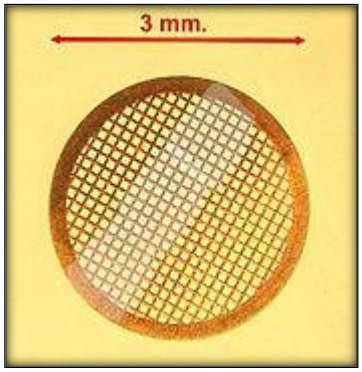


Figure-1.40.TEM sample support mesh "grid", with ultramicrotomy sections

This grid is placed into the sample holder which is paired with the specimen stage. A wide variety of designs of stages and holders exist, depending upon the type of experiment being performed. In addition to 3.05 mm grids, 2.3 mm grids are sometimes, if rarely, used. These grids were particularly used in the mineral sciences where a large degree of tilt can be required and where specimen material may be extremely rare. Electron transparent specimens have a thickness around 100 nm, but this value depends on the accelerating voltage.

Once inserted into a TEM, the sample often has to be manipulated to present the region of interest to the beam, such as in single grain diffraction, in a specific orientation. To accommodate this, the TEM stage includes mechanisms for the translation of the sample in the XY plane of the sample, for Z height adjustment of the sample holder, and usually for at least one rotation degree of freedom for the sample. Thus a TEM stage may provide four degrees of freedom for the motion of the specimen. Most modern TEMs provide the ability

for two orthogonal rotation angles of movement with specialized holder designs called double-tilt sample holders. Of note however is that some stage designs, such as top-entry or vertical insertion stages once common for high resolution TEM studies, may simply only have X-Y translation available. The design criteria of TEM stages are complex, owing to the simultaneous requirements of mechanical and electron-optical constraints and have thus generated many unique implementations.

A TEM stage is required to have the ability to hold a specimen and be manipulated to bring the region of interest into the path of the electron beam. As the TEM can operate over a wide range of magnifications, the stage must simultaneously be highly resistant to mechanical drift, with drift requirements as low as a few nm/minute while being able to move several um/minute, with repositioning accuracy on the order of nanometers. Earlier designs of TEM accomplished this with a complex set of mechanical downgearing devices, allowing the operator to finely control the motion of the stage by several rotating rods. Modern devices may use electrical stage designs, using screw gearing in concert with stepper motors, providing the operator with a computer-based stage input, such as a joystick or trackball.

Two main designs for stages in a TEM exist, the side-entry and top entry version. Each design must accommodate the matching holder to allow for specimen insertion without either damaging delicate TEM optics or allowing gas into TEM systems under vacuum.

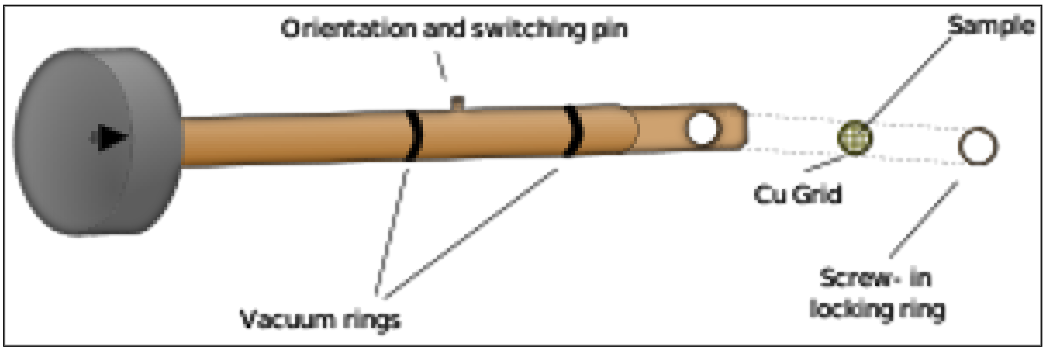


Figure-1.41.A diagram of a single axis tilt sample holder for insertion into a TEM goniometer. Titling of the holder is achieved by rotation of the entire goniometer

The most common is the side entry holder, where the specimen is placed near the tip of a long metal (brass or stainless steel) rod, with the specimen placed flat in a small bore. Along the rod are several polymer vacuum rings to allow for the formation of a vacuum seal of sufficient quality, when inserted into the stage. The stage is thus designed to accommodate the rod, placing the sample either in between or near the objective lens, dependent upon the objective design. When inserted into the stage, the side entry holder has its tip contained within the TEM vacuum, and the base is presented to atmosphere, the airlock formed by the vacuum rings.

Insertion procedures for side entry TEM holders typically involve the rotation of the sample to trigger micro switches that initiate evacuation of the airlock before the sample is inserted into the TEM column.

The second design is the top-entry holder consists of a cartridge that is several cm long with a bore drilled down the cartridge axis. The specimen is loaded into the bore, possibly utilising a

small screw ring to hold the sample in place. This cartridge is inserted into an airlock with the bore perpendicular to the TEM optic axis. When sealed, the airlock is manipulated to push the cartridge such that the cartridge falls into place, where the bore hole becomes aligned with the beam axis, such that the beam travels down the cartridge bore and into the specimen. Such designs are typically unable to be tilted without blocking the beam path or interfering with the objective lens.

Electron gun

The electron gun is formed from several components: the filament, a biasing circuit, a Wehnelt cap, and an extraction anode. By connecting the filament to the negative component power supply, electrons can be "pumped" from the electron gun to the anode plate, and TEM column, thus completing the circuit. The gun is designed to create a beam of electrons exiting from the assembly at some given angle, known as the gun divergence semiangle, α.

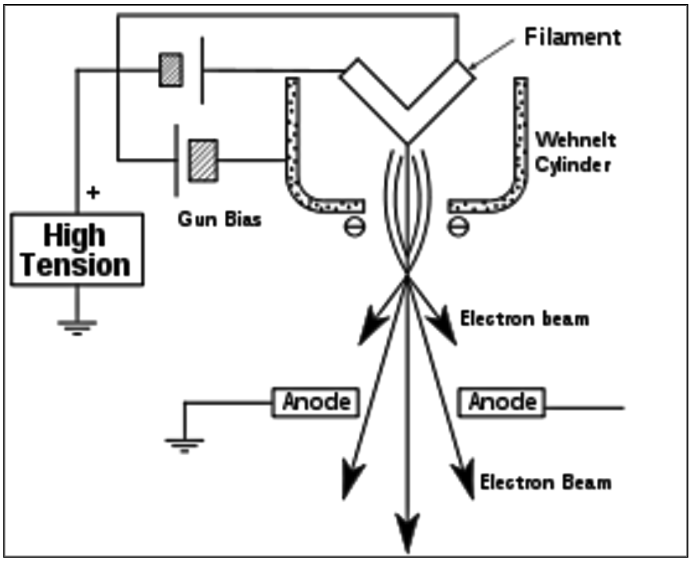


Figure-1.42.Cross sectional diagram of an electron gun assembly, illustrating electron extraction

By constructing the Wehnelt cylinder such that it has a higher negative charge than the filament itself, electrons that exit the filament in a diverging manner are, under proper operation, forced into a converging pattern the minimum size of which is the gun crossover diameter. The thermionic emission current density, J, can be related to the work function of the emitting material and is a Boltzmann distribution given below, where A is a constant, Φ is the work function and T is the temperature of the material.

$$J = AT^2 \exp\left(-\frac{\Phi}{kT}\right)$$

This equation shows that in order to achieve sufficient current density it is necessary to heat the emitter, taking care not to cause damage by application of excessive heat, for this reason materials with either a high melting point, such as tungsten, or those with a low work function (LaB_6) are required for the gun filament.[25] Furthermore both lanthanum hexaboride and tungsten thermionic sources must be heated in order to achieve thermionic emission, this

can be achieved by the use of a small resistive strip. To prevent thermal shock, there is often a delay enforced in the application of current to the tip, to prevent thermal gradients from damaging the filament, the delay is usually a few seconds for LaB_6, and significantly lower for tungsten.

Electron lens

Electron lenses are designed to act in a manner emulating that of an optical lens, by focusing parallel rays at some constant focal length. Lenses may operate electrostatically or magnetically. The majority of electron lenses for TEM utilise electromagnetic coils to generate a convex lens. For these lenses the field produced for the lens must be radially symmetric, as deviation from the radial symmetry of the magnetic lens causes aberrations such as astigmatism, and worsens spherical and chromatic aberration. Electron lenses are manufactured from iron, iron-cobalt or nickel cobalt alloys, such as permalloy. These are selected for their magnetic properties, such as magnetic saturation, hysteresis and permeability.

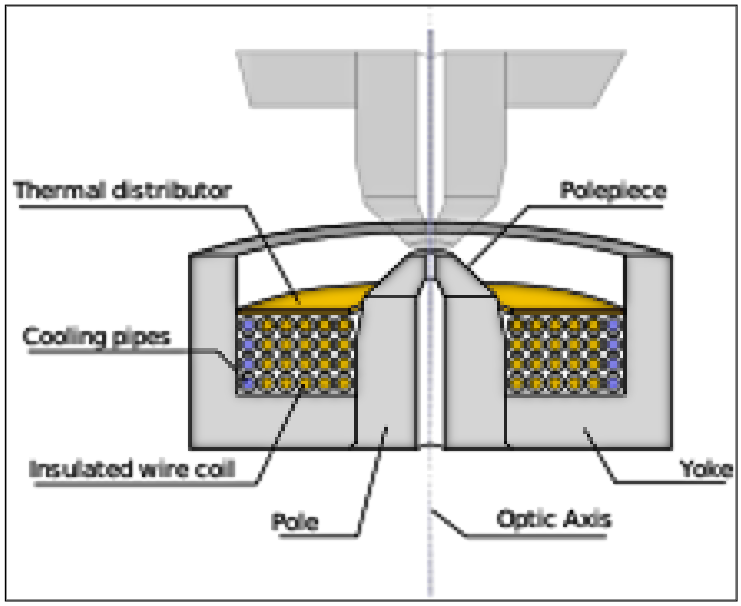


Figure-1.43.Diagram of a TEM split polepiece design lens

The components include the yoke, the magnetic coil, the poles, the polepiece, and the external control circuitry. The polepiece must be manufactured in a very symmetrical manner, as this provides the boundary conditions for the magnetic field that forms the lens. Imperfections in the manufacture of the polepiece can induce severe distortions in the magnetic field symmetry, which induce distortions that will ultimately limit the lenses' ability to reproduce the object plane. The exact dimensions of the gap, pole piece internal diameter and taper, as well as the overall design of the lens is often performed by finite element analysis of the magnetic field, whilst considering the thermal and electrical constraints of the design.

The coils which produce the magnetic field are located within the lens yoke. The coils can contain a variable current, but typically utilise high voltages, and therefore require significant insulation in order to prevent short-circuiting the lens components. Thermal distributors are placed to ensure the extraction of the heat generated by the energy lost to resistance of the

coil windings. The windings may be water-cooled, using a chilled water supply in order to facilitate the removal of the high thermal duty.

Apertures

Apertures are annular metallic plates, through which electrons that are further than a fixed distance from the optic axis may be excluded. These consist of a small metallic disc that is sufficiently thick to prevent electrons from passing through the disc, whilst permitting axial electrons. This permission of central electrons in a TEM causes two effects simultaneously: firstly, apertures decrease the beam intensity as electrons are filtered from the beam, which may be desired in the case of beam sensitive samples. Secondly, this filtering removes electrons that are scattered to high angles, which may be due to unwanted processes such as spherical or chromatic aberration, or due to diffraction from interaction within the sample.

Apertures are either a fixed aperture within the column, such as at the condensor lens, or are a movable aperture, which can be inserted or withdrawn from the beam path, or moved in the plane perpendicular to the beam path. Aperture assemblies are mechanical devices which allow for the selection of different aperture sizes, which may be used by the operator to trade off intensity and the filtering effect of the aperture. Aperture assemblies are often equipped with micrometers to move the aperture, required during optical calibration.

Imaging methods

Imaging methods in TEM utilize the information contained in the electron waves exiting from the sample to form an image. The projector lenses allow for the correct positioning of this electron wave distribution onto the viewing system. The observed intensity of the image, I, assuming sufficiently high quality of imaging device, can be approximated as proportional to the time-average amplitude of the electron wavefunctions, where the wave which form the exit beam is denoted by Ψ

$$I(x) = \frac{k}{t_1 - t_0} \int_{t_0}^{t_1} \Psi \Psi^* \, dt$$

Different imaging methods therefore attempt to modify the electron waves exiting the sample in a form that is useful to obtain information with regards to the sample, or beam itself. From the previous equation, it can be deduced that the observed image depends not only on the amplitude of beam, but also on the phase of the electrons, although phase effects may often be ignored at lower magnifications. Higher resolution imaging requires thinner samples and higher energies of incident electrons. Therefore the sample can no longer be considered to be absorbing electrons, via a Beer's law effect, rather the sample can be modelled as an object that does not change the amplitude of the incoming electron wavefunction. Rather the sample modifies the phase of the incoming wave; this model is known as a pure phase object, for sufficiently thin specimens phase effects dominate the image, complicating analysis of the observed intensities. For example, to improve the contrast in the image the TEM may be operated at a slight defocus to enhance contrast, owing to convolution by the contrast transfer function of the TEM, which would normally decrease contrast if the sample was not a weak phase object.

Contrast formation

Contrast formation in the TEM depends greatly on the mode of operation. Complex imaging techniques, which utilise the unique ability to change lens strength or to deactivate a lens, allow for many operating modes. These modes may be used to discern information that is of particular interest to the investigator.

Bright field

The most common mode of operation for a TEM is the bright field imaging mode. In this mode the contrast formation, when considered classically, is formed directly by occlusion and absorption of electrons in the sample. Thicker regions of the sample, or regions with a higher atomic number will appear dark, whilst regions with no sample in the beam path will appear bright – hence the term "bright field". The image is in effect assumed to be a simple two dimensional projection of the sample down the optic axis, and to a first approximation may be modelled via Beer's law, more complex analyses require the modelling of the sample to include phase information.

Diffraction contrast

Samples can exhibit diffraction contrast, whereby the electron beam undergoes Bragg scattering, which in the case of a crystalline sample, disperses electrons into discrete locations in the back focal plane. By the placement of apertures in the back focal plane, i.e. the objective aperture, the desired Bragg reflections can be selected (or excluded), thus only parts of the sample that are causing the electrons to scatter to the selected reflections will end up projected onto the imaging apparatus.

Figure-1.44.Transmission electron micrograph of dislocations in steel, which are faults in the structure of the crystal lattice at the atomic scale

If the reflections that are selected do not include the unscattered beam (which will appear up at the focal point of the lens), then the image will appear dark wherever no sample scattering to the selected peak is present, as such a region without a specimen will appear dark. This is known as a dark-field image.

Modern TEMs are often equipped with specimen holders that allow the user to tilt the specimen to a range of angles in order to obtain specific diffraction conditions, and apertures placed above the specimen allow the user to select electrons that would otherwise be diffracted in a particular direction from entering the specimen.

Applications for this method include the identification of lattice defects in crystals. By carefully selecting the orientation of the sample, it is possible not just to determine the position of defects but also to determine the type of defect present. If the sample is oriented so that one particular plane is only slightly tilted away from the strongest diffracting angle (known as the Bragg Angle), any distortion of the crystal plane that locally tilts the plane to the Bragg angle will produce particularly strong contrast variations. However, defects that produce only displacement of atoms that do not tilt the crystal to the Bragg angle (i. e. displacements parallel to the crystal plane) will not produce strong contrast.

Electron Energy Loss

Utilizing the advanced technique of EELS, for TEMs appropriately equipped electrons can be rejected based upon their voltage (which, due to constant charge is their energy), using magnetic sector based devices known as EELS spectrometers. These devices allow for the selection of particular energy values, which can be associated with the way the electron has interacted with the sample. For example different elements in a sample result in different electron energies in the beam after the sample. This normally results in chromatic aberration however this effect can, for example, be used to generate an image which provides information on elemental composition, based upon the atomic transition during electron-electron interaction.

EELS spectrometers can often be operated in both spectroscopic and imaging modes, allowing for isolation or rejection of elastically scattered beams. As for many images inelastic scattering will include information that may not be of interest to the investigator thus reducing observable signals of interest, EELS imaging can be used to enhance contrast in observed images, including both bright field and diffraction, by rejecting unwanted components.

Phase contrast

Crystal structure can also be investigated by high-resolution transmission electron microscopy (HRTEM), also known as phase contrast. When utilizing a Field emission source, of uniform thickness, the images are formed due to differences in phase of electron waves, which is caused by specimen interaction. Image formation is given by the complex modulus of the incoming electron beams. As such, the image is not only dependent on the number of electrons hitting the screen, making direct interpretation of phase contrast images more complex. However this effect can be used to an advantage, as it can be manipulated to provide more information about the sample, such as in complex phase retrieval techniques.

Diffraction

As previously stated, by adjusting the magnetic lenses such that the back focal plane of the lens rather than the imaging plane is placed on the imaging apparatus a diffraction pattern can be generated. For thin crystalline samples, this produces an image that consists of a pattern of dots in the case of a single crystal, or a series of rings in the case of a polycrystalline or amorphous solid material. For the single crystal case the diffraction pattern is dependent upon the orientation of the specimen and the structure of the sample illuminated by the electron beam. This image provides the investigator with information about the space group symmetries in the crystal and the crystal's orientation to the beam path. This is typically done

without utilising any information but the position at which the diffraction spots appear and the observed image symmetries.

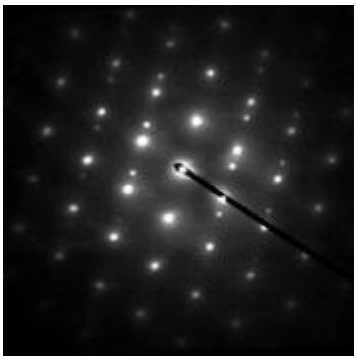


Figure-1.45.Crystalline diffraction pattern from a twinned grain of FCC Austenitic steel

Diffraction patterns can have a large dynamic range, and for crystalline samples, may have intensities greater than those recordable by CCD. As such, TEMs may still be equipped with film cartridges for the purpose of obtaining these images, as the film is a single use detector.

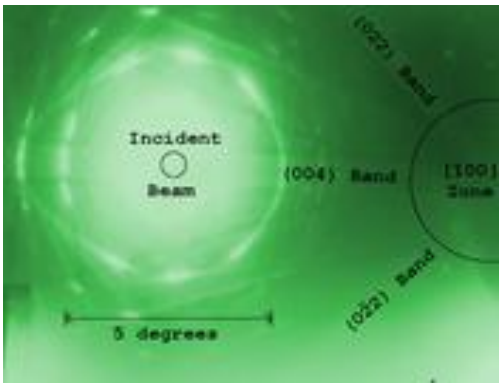


Figure-1.46.Convergent Beam Kikuchi lines from Silicon, near the [100] zone axis

Analysis of diffraction patterns beyond point-position can be complex, as the image is sensitive to a number of factors such as specimen thickness and orientation, objective lens defocus, spherical and chromatic aberration. Although quantitative interpretation of the contrast shown in lattice images is possible, it is inherently complicated and can require extensive computer simulation and analysis, such as electron multislice analysis.

More complex behaviour in the diffraction plane is also possible, with phenomena such as Kikuchi lines arising from multiple diffraction within the crystalline lattice. In convergent beam electron diffraction (CBED) where a non-parallel, i.e. converging, electron wavefront is produced by concentrating the electron beam into a fine probe at the sample surface, the interaction of the convergent beam can provide information beyond structural data such as sample thickness.

Three-dimensional imaging

As TEM specimen holders typically allow for the rotation of a sample by a desired angle, multiple views of the same specimen can be obtained by rotating the angle of the sample along an axis perpendicular to the beam. By taking multiple images of a single TEM sample at differing angles, typically in 1° increments, a set of images known as a "tilt series" can be collected. This methodology was proposed in the 1970s by Walter Hoppe. Under purely absorption contrast conditions, this set of images can be used to construct a three-dimensional representation of the sample.

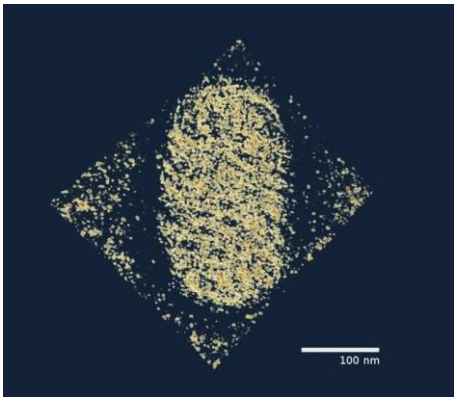


Figure-1.47.A three-dimensional TEM image of a parapoxavirus

The reconstruction is accomplished by a two-step process, first images are aligned to account for errors in the positioning of a sample; such errors can occur due to vibration or mechanical drift. Alignment methods use image registration algorithms, such as autocorrelation methods to correct these errors. Secondly, using a technique known as filtered back projection, the aligned image slices can be transformed from a set of two-dimensional images, $I_j(x, y)$, to a single three-dimensional image, $I'_j(x, y, z)$. This three-dimensional image is of particular interest when morphological information is required, further study can be undertaken using computer algorithms, such as isosurfaces and data slicing to analyse the data.

As TEM samples cannot typically be viewed at a full 180° rotation, the observed images typically suffer from a "missing wedge" of data, which when using Fourier-based back projection methods decreases the range of resolvable frequencies in the three-dimensional reconstruction. Mechanical refinements, such as multi-axis tilting (two tilt series of the same specimen made at orthogonal directions) and conical tomography (where the specimen is first tilted to a given fixed angle and then imaged at equal angular rotational increments through one complete rotation in the plane of the specimen grid) can be used to limit the impact of the missing data on the observed specimen morphology. In addition, numerical techniques exist which can improve the collected data.

All the above-mentioned methods involve recording tilt series of a given specimen field. This inevitably results in the summation of a high dose of reactive electrons through the sample and the accompanying destruction of fine detail during recording. The technique of low-dose (minimal-dose) imaging is therefore regularly applied to mitigate this effect. Low-dose imaging is performed by deflecting illumination and imaging regions simultaneously away from the optical axis to image an adjacent region to the area to be recorded (the high-dose region). This area is maintained centred during tilting and refocused before recording. During

recording the deflections are removed so that the area of interest is exposed to the electron beam only for the duration required for imaging. An improvement of this technique (for objects resting on a sloping substrate film) is to have two symmetrical off-axis regions for focusing followed by setting focus to the average of the two high-dose focus values before recording the low-dose area of interest.

Non-tomographic variants on this method, referred to as single particle analysis, use images of multiple (hopefully) identical objects at different orientations to produce the image data required for three-dimensional reconstruction. If the objects do not have significant preferred orientations, this method does not suffer from the missing data wedge (or cone) which accompany tomographic methods nor does it incur excessive radiation dosage, however it assumes that the different objects imaged can be treated as if the 3D data generated from them arose from a single stable object.

Sample preparation

Sample preparation in TEM can be a complex procedure. TEM specimens are required to be at most hundreds of nanometers thick, as unlike neutron or X-Ray radiation the electron beam interacts readily with the sample, an effect that increases roughly with atomic number squared (z^2). High quality samples will have a thickness that is comparable to the mean free path of the electrons that travel through the samples, which may be only a few tens of nanometers. Preparation of TEM specimens is specific to the material under analysis and the desired information to obtain from the specimen. As such, many generic techniques have been used for the preparation of the required thin sections.

Materials that have dimensions small enough to be electron transparent, such as powders or nanotubes, can be quickly prepared by the deposition of a dilute sample containing the specimen onto support grids or films. In the biological sciences in order to withstand the instrument vacuum and facilitate handling, biological specimens can be fixated using either a negative staining material such as uranyl acetate or by plastic embedding. Alternately samples may be held at liquid nitrogen temperatures after embedding in vitreous ice.[35] In material science and metallurgy the specimens tend to be naturally resistant to vacuum, but still must be prepared as a thin foil, or etched so some portion of the specimen is thin enough for the beam to penetrate. Constraints on the thickness of the material may be limited by the scattering cross-section of the atoms from which the material is comprised.

Tissue sectioning

By passing samples over a glass or diamond edge, small, thin sections can be readily obtained using a semi-automated method. This method is used to obtain thin, minimally deformed samples that allow for the observation of tissue samples. Additionally inorganic samples have been studied, such as aluminium, although this usage is limited owing to the heavy damage induced in the less soft samples. To prevent charge build-up at the sample surface, tissue samples need to be coated with a thin layer of conducting material, such as carbon, where the coating thickness is several nanometers. This may be achieved via an electric arc deposition process using a sputter coating device.

Sample staining

Details in light microscope samples can be enhanced by stains that absorb light; similarly TEM samples of biological tissues can utilize high atomic number stains to enhance contrast. The stain absorbs electrons or scatters part of the electron beam which otherwise is projected onto the imaging system.

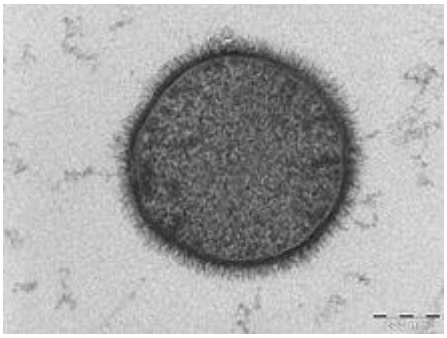


Figure-1.48.A section of a cell of Bacillus subtilis, taken with a Tecnai T-12 TEM. The scale bar is 200 nm.

Compounds of heavy metals such as osmium, lead, uranium or gold (in immunogold labelling) may be used prior to TEM observation to selectively deposit electron dense atoms in or on the sample in desired cellular or protein regions, requiring an understanding of how heavy metals bind to biological tissues.

Mechanical milling

Mechanical polishing may be used to prepare samples. Polishing needs to be done to a high quality, to ensure constant sample thickness across the region of interest. A diamond, or cubic boron nitride polishing compound may be used in the final stages of polishing to remove any scratches that may cause contrast fluctuations due to varying sample thickness. Even after careful mechanical milling, additional fine methods such as ion etching may be required to perform final stage thinning.

Chemical etching

Certain samples may be prepared by chemical etching, particularly metallic specimens. These samples are thinned using a chemical etchant, such as an acid, to prepare the sample for TEM observation. Devices to control the thinning process may allow the operator to control either the voltage or current passing through the specimen, and may include systems to detect when the sample has been thinned to a sufficient level of optical transparency.

Ion etching

Ion etching is a sputtering process that can remove very fine quantities of material. This is used to perform a finishing polish of specimens polished by other means. Ion etching uses an inert gas passed through an electric field to generate a plasma stream that is directed to the sample surface. Acceleration energies for gases such as argon are typically a few kilovolts.

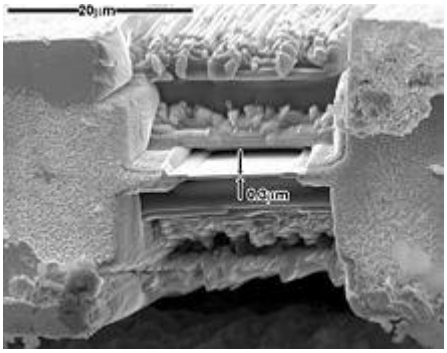


Figure-1.49.SEM image of a thin TEM sample milled by FIB. The thin membrane shown here is suitable for TEM examination; however, at ~300-nm thick, it would not be suitable for high-resolution TEM without further milling.

The sample may be rotated to promote even polishing of the sample surface. The sputtering rate of such methods is on the order of tens of micrometers per hour, limiting the method to only extremely fine polishing.

More recently focused ion beam methods have been used to prepare samples. FIB is a relatively new technique to prepare thin samples for TEM examination from larger specimens. Because FIB can be used to micro-machine samples very precisely, it is possible to mill very thin membranes from a specific area of interest in a sample, such as a semiconductor or metal. Unlike inert gas ion sputtering, FIB makes use of significantly more energetic gallium ions and may alter the composition or structure of the material through gallium implantation.

Replication

Samples may also be replicated using cellulose acetate film, the film subsequently coated with a heavy metal, the original film melted away, and the replica imaged on the TEM. This technique is used for both materials and biological samples.

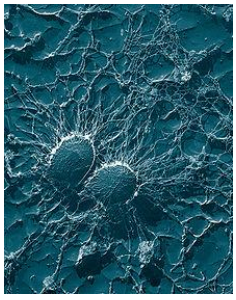


Figure-1.50.Staphylococcus aureus platinum replica image shot on a TEM at 50,000X magnification

Modifications

The capabilities of the TEM can be further extended by additional stages and detectors, sometimes incorporated on the same microscope. An electron cryomicroscope (CryoTEM) is a TEM with a specimen holder capable of maintaining the specimen at liquid nitrogen or

liquid helium temperatures. This allows imaging specimens prepared in vitreous ice, the preferred preparation technique for imaging individual molecules or macromolecular assemblies. A TEM can be modified into a scanning transmission electron microscope (STEM) by the addition of a system that rasters the beam across the sample to form the image, combined with suitable detectors. Scanning coils are used to deflect the beam, such as by an electrostatic shift of the beam, where the beam is then collected using a current detector such as a faraday cup, which acts as a direct electron counter. By correlating the electron count to the position of the scanning beam (known as the "probe"), the transmitted component of the beam may be measured. The non-transmitted components may be obtained either by beam tilting or by the use of annular dark field detectors. In-situ experiments may also be conducted with experiments such as in-situ reactions or material deformation testing.

Modern research TEMs may include aberration correctors, to reduce the amount of distortion in the image. Incident beam Monochromators may also be used which reduce the energy spread of the incident electron beam to less than 0.15 eV. Major TEM makers include JEOL, Hitachi High-technologies, FEI Company (from merging with Philips Electron Optics), Carl Zeiss and NION.

Low-voltage electron microscope (LVEM)

The low-voltage electron microscope (LVEM) is a combination of SEM, TEM and STEM in one instrument, which operated at relatively low electron accelerating voltage of 5 kV. Low voltage increases image contrast which is especially important for biological specimens. This increase in contrast significantly reduces, or even eliminates the need to stain. Sectioned samples generally need to be thinner than they would be for conventional TEM (20-65 nm). Resolutions of a few nm are possible in TEM, SEM and STEM modes.

Cryo-Electron Microscopy

This technique allows TEM's to be used to see molecular structure of proteins and large molecules. Cryoelectron microscopy involves viewing unaltered macromolecular assemblies by vitrifying them, placing them on a grid and obtaining images by detecting electrons that transmit through the specimen.

Limitations

There are a number of drawbacks to the TEM technique. Many materials require extensive sample preparation to produce a sample thin enough to be electron transparent, which makes TEM analysis a relatively time consuming process with a low throughput of samples. The structure of the sample may also be changed during the preparation process. Also the field of view is relatively small, raising the possibility that the region analyzed may not be characteristic of the whole sample. There is potential that the sample may be damaged by the electron beam, particularly in the case of biological materials.

Resolution limits

The limit of resolution obtainable in a TEM may be described in several ways, and is typically referred to as the information limit of the microscope.

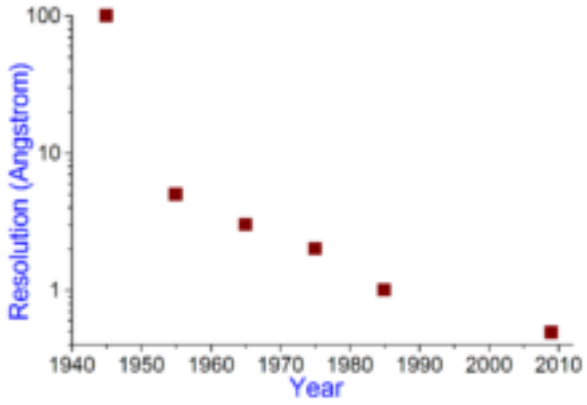


Figure-1.51.Approximate tendency of spatial resolution achieved with TEM

One commonly used value is a cut-off value of the contrast transfer function, a function that is usually quoted in the frequency domain to define the reproduction of spatial frequencies of objects in the object plane by the microscope optics. A cut-off frequency, q_{max}, for the transfer function may be approximated with the following equation, where C_s is the spherical aberration coefficient and λ is the electron wavelength.

$$q_{\max} = \frac{1}{0.67(C_s\lambda^3)^{1/4}}.$$

For a 200 kV microscope, with partly corrected spherical aberrations ("to the third order") and a C_s value of 1 µm, a theoretical cut-off value might be $1/q_{max}$ = 42 pm. The same microscope without a corrector would have C_s = 0.5 mm and thus a 200-pm cut-off. The spherical aberrations are suppressed to the third or fifth order in the "aberration-corrected" microscopes. Their resolution is however limited by electron source geometry and brightness and chromatic aberrations in the objective lens system. The frequency domain representation of the contrast transfer function may often have an oscillatory nature, which can be tuned by adjusting the focal value of the objective lens. This oscillatory nature implies that some spatial frequencies are faithfully imaged by the microscope, whilst others are suppressed. By combining multiple images with different spatial frequencies, the use of techniques such as focal series reconstruction can be used to improve the resolution of the TEM in a limited manner. The contrast transfer function can, to some extent, be experimentally approximated through techniques such as Fourier transforming images of amorphous material, such as amorphous carbon. More recently, advances in aberration corrector design have been able to reduce spherical aberrations and to achieve resolution below 0.5 Ångströms (50 pm) 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.

1.9. Applications of Nanotechnology

The tip of a scanning probe can also be used to manipulate nanostructures (a process called positional assembly). Feature-oriented scanning methodology suggested by Rostislav Lapshin appears to be a promising way to implement these nanomanipulations in automatic mode. **[26, 27]** However, this is still a slow process because of low scanning velocity of the microscope. Various techniques of nanolithography such as optical lithography, X-ray lithography 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. Another group of nanotechnological techniques include those used for fabrication of nanotubes and 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 vapour 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. The top-down approach anticipates nanodevices that must be built piece by piece in stages, much as manufactured items are made. Scanning probe microscopy is an important technique both for characterization and synthesis of nanomaterial.

Atomic force microscopes and scanning tunnelling 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 approach, atoms or molecules can be moved around on a surface with scanning probe microscopy techniques. **[26, 27]** 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. Dual polarisation interferometer is one tool suitable for characterisation of self assembled thin films. 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. However, new therapeutic products, based on responsive nanomaterial, such as the ultra deformable, stress-sensitive Transfer some vesicles, are under development and already approved for human use in some countries.

As of August 21, 2008, the Project on Emerging Nanotechnologies estimates that over 800 manufacturer-identified nanotech products is publicly available, with new ones hitting the market at a pace of 3–4 per week. The project lists all of the products in a publicly accessible online database. Most applications are limited to the use of "first generation" passive nanomaterial which includes titanium dioxide in sunscreen, cosmetics, surface coatings, **[28]** and some food products; Carbon allotropes used to produce gecko tape; silver in food packaging, clothing, disinfectants and household appliances; zinc oxide in sunscreens and cosmetics, surface coatings, paints and outdoor furniture varnishes; and cerium oxide as a fuel catalyst. **[7].**

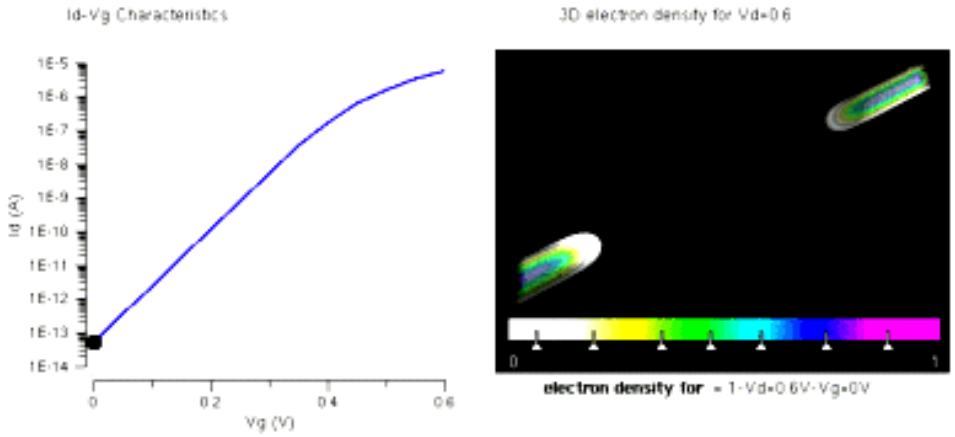


Figure-1.52.One of the major applications of nanotechnology is in the area of nanoelectronics with MOSFET's being made of small nanowires ~10 nm in length.

Here is a simulation of such a nanowire Further applications allow tennis balls to last longer, golf balls to fly straighter, and even bowling balls to become more durable and have a harder surface. Trousers and socks have been infused with nanotechnology so that they will last longer and keep people cool in the summer. Bandages are being infused with silver nanoparticles to heal cuts faster. Cars are being manufactured with nanomaterial so they may need fewer metals and less fuel to operate in the future. Video game consoles and personal computers may become cheaper, faster, and contain more memory thanks to nanotechnology. Nanotechnology may have the ability to make existing medical applications cheaper and easier to use in places like the general practitioner's office and at home. The National Science Foundation (a major distributor for nanotechnology research in the United States) funded researcher David Be rube to study the field of nanotechnology. His findings are published in the monograph Nano-Hype: The Truth behind the Nanotechnology Buzz. This study concludes that much of what is sold as “nanotechnology” is in fact a recasting of straightforward materials science, which is leading to a “nanotech industry built solely on selling nanotubes, nanowires, and the like” which will “end up with a few suppliers selling low margin products in huge volumes." Further applications which require actual manipulation or arrangement of nanoscale components await further research. Though technologies branded with the term 'nano' are sometimes little related to and fall far short of the most ambitious and transformative technological goals of the sort in molecular manufacturing proposals, the term still connotes such ideas. According to Be rube, there may be a danger that a "nano bubble" will form, or is forming already, from the use of the term by scientists and entrepreneurs to garner funding, regardless of interest in the transformative possibilities of more ambitious and far-sighted work. **[29]**

1.10. Current research

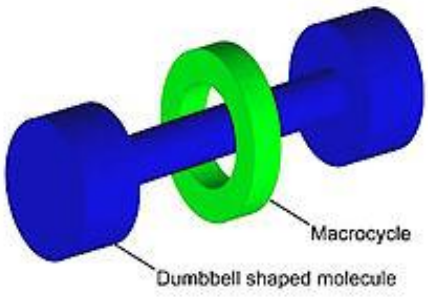


Figure-1.53.Graphical representation of a rotaxane, useful as a molecular switch.

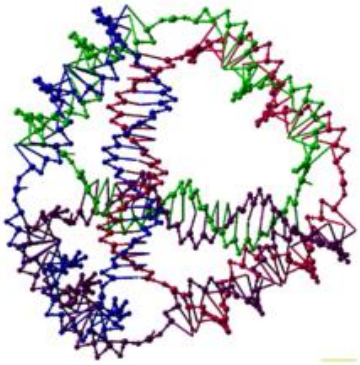


Figure-1.54.DNA tetrahedron [15]

Is an artificially designed nanostructure of the type made in the field of DNA nanotechnology. Each edge of the tetrahedron is a 20 base pair DNA double helix, and each vertex is a three-arm junction.

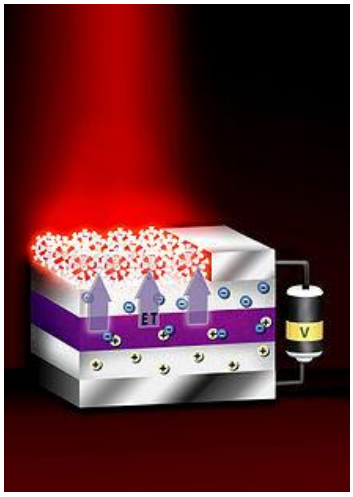


Figure-1.55.Device transfers energy from nano-thin layers of quantum wells to nanocrystals above them, causing the nanocrystals to emit visible light.

Interdigitated Nanoelectrodes for Nanoparticle Detection

Electrodes can be fabricated with electron beam lithography to have precise gaped and shaped electrodes. Connection of these electrodes could indicate the presence of a specific compound.

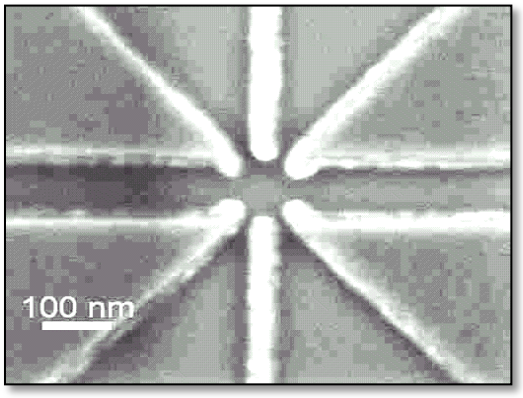


Figure-1.56.Interdigitated Nanoelectrodes

Nanomachines are largely in the research-and-development phase

But some primitive devices have been tested. An example is a sensor having a switch approximately 1.5 nanometers across, capable of counting specific molecules in a chemical sample. The first useful applications of nanomachines will likely be in medical technology, where they could be used to identify pathogens and toxins from samples of body fluid and destroy them. Another potential application is the detection of toxic chemicals, and the measurement of their concentrations, in the environment. Recently, Rice University has demonstrated a single-molecule car, which is developed by a chemical process and includes buckyballs for wheels. It is actuated by controlling the environmental temperature and by positioning a scanning tunneling microscope tip.

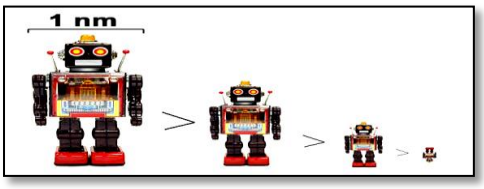
Recently groups have found they can use the STM tip to rotate individual bonds within single molecules. The electrical resistance of the molecule depends on the orientation of the bond, so the molecule effectively becomes a molecular switch.

Nanodots

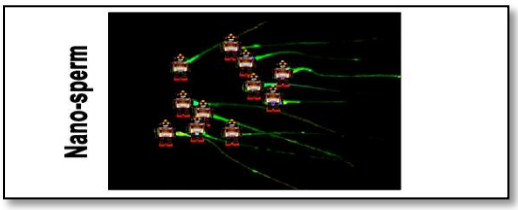
Nanodots and quantum dots are small lifted pieces of raised surface up to several atoms thick that are created by attaching atoms to the SPM tip so that a strip of atoms are lifted and then deposited again. This is a little like pulling a bit of plasticine from a surface to make a bump. Using a platinum tip, nanodots of about 1-2 nm in diameter have been created. Nanodots are useful in molecular computing.

Predictions of Nanodots in future

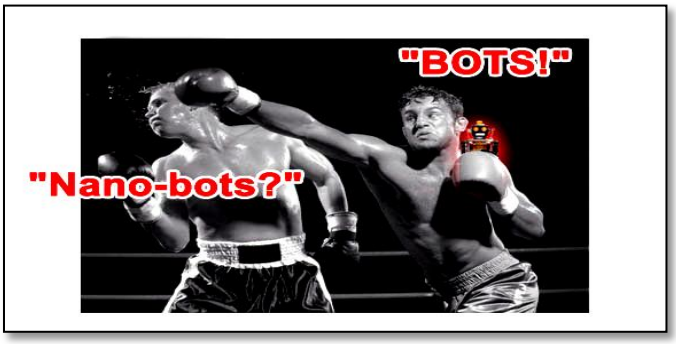
1. Nanobots will create a new civilization with advanced technology and develop their own even smaller nanobots.



2. Every fluid in your body: blood, saliva, bile, even semen, will be replaced by nanobots.



3. Nanobots will drive the regular-sized robot market in to the ground until they are obsolete. After this occurs, nanobots will simply be referred to as "bots



4. A nanobot virus will be created that will cause people to do "the robot" without stopping until they die a horrible deaths.

1.11. Implications

The Centre for Responsible Nanotechnology warns of the broad societal implications of untraceable weapons of mass destruction, networked cameras for use by the government, and weapons developments fast enough to destabilize arms races. Another area of concern is the

effect that industrial-scale manufacturing and use of nanomaterial would have on human health and the environment, as suggested by nanotoxicology research. For these reasons, groups such as the Centre for Responsible Nanotechnology advocate that nanotechnology be regulated by governments. Others counter that overregulation would stifle scientific research and the development of beneficial innovations. Some nanoparticle products may have unintended consequences. Researchers have discovered that bacteriostatic silver nanoparticles used in socks to reduce foot odor are being released in the wash. These particles are then flushed into the waste water stream and may destroy bacteria which are critical components of natural ecosystems, farms, and waste treatment processes **[30].** Public deliberations on risk perception in the US and UK carried out by the Centre for Nanotechnology in Society found that participants were more positive about nanotechnologies for energy applications than for health applications, with health applications raising moral and ethical dilemmas such as cost and availability. **[31]** Experts, including director of the Woodrow Wilson Centre's Project on Emerging Nanotechnologies David Rejeski, have testified **[32]** that successful commercialization depends on adequate oversight, risk research strategy, and public engagement. Berkeley, California is currently the only city in the United States to regulate nanotechnology**.** Cambridge, Massachusetts in 2008 considered enacting a similar law, **[33]** but ultimately rejected it. **[34]** Relevant for both research on and application of nanotechnologies, the insurability of nanotechnology is contested. **[35]** Without state regulation of nanotechnology, the availability of private insurance for potential damages is seen as necessary to ensure that burdens are not socialised implicitly.

1.12. Health and environmental concerns

Researchers have found that when rats breathed in nanoparticles, the particles settled in the brain and lungs, which led to significant increases in biomarkers for inflammation and stress response and those nanoparticles, induce skin aging through oxidative stress in hairless mice **[36, 37].** A two-year study at UCLA's School of Public Health found lab mice consuming nano-titanium dioxide showed DNA and chromosome damage to a degree "linked to all the big killers of man, namely cancer, heart disease, neurological disease and aging".**[38].** A major study published more recently in Nature Nanotechnology suggests some forms of carbon nanotubes – a poster child for the "nanotechnology revolution" – could be as harmful as asbestos if inhaled in sufficient quantities. Anthony Seaton of the Institute of Occupational Medicine in Edinburgh, Scotland, who contributed to the article on carbon nanotubes, said "We know that some of them probably have the potential to cause mesothelioma. So those sorts of materials need to be handled very carefully." **[39]** In the absence of specific regulation forthcoming from governments, Paull and Lyons (2008) have called for an exclusion of engineered nanoparticles in food. **[40]** A newspaper article reports that workers in a paint factory developed serious lung disease and nanoparticles were found in their lungs**. [41]**

1.13. Regulation

Calls for tighter regulation of nanotechnology have occurred alongside a growing debate related to the human health and safety risks of nanotechnology. **[42]** There is significant debate about who is responsible for the regulation of nanotechnology. Some regulatory agencies currently cover some nanotechnology products and processes (to varying degrees) – by "bolting on" nanotechnology to existing regulations – there are clear gaps in these regimes. **[43]** Davies (2008) has proposed a regulatory road map describing steps to deal with

these shortcomings. **[44].** Stakeholders concerned by the lack of a regulatory framework to assess and control risks associated with the release of nanoparticles and nanotubes have drawn parallels with bovine spongiform encephalopathy ("mad cow" disease), thalidomide, genetically modified food, **[45]** nuclear energy, reproductive technologies, biotechnology, and asbestosis. Dr. Andrew Maynard, chief science advisor to the Woodrow Wilson Centre's Project on Emerging Nanotechnologies, concludes that there is insufficient funding for human health and safety research, and as a result there is currently limited understanding of the human health and safety risks associated with nanotechnology. **[46]** As a result, some academics have called for stricter application of the precautionary principle, with delayed marketing approval, enhanced labelling and additional safety data development requirements in relation to certain forms of nanotechnology. **[47].** The Royal Society report **[5]** identified a risk of nanoparticles or nanotubes being released during disposal, destruction and recycling, and recommended that "manufacturers of products that fall under extended producer responsibility regimes such as end-of-life regulations publish procedures outlining how these materials will be managed to minimize possible human and environmental exposure" (p. xiii). Reflecting the challenges for ensuring responsible life cycle regulation, the Institute for Food and Agricultural Standards has proposed that standards for nanotechnology research and development should be integrated across consumer, worker and environmental standards. They also propose that NGOs and other citizen groups play a meaningful role in the development of these standards. The Centre for Nanotechnology in Society has found that people respond differently to nanotechnologies based upon application – with participants in public deliberations more positive about nanotechnologies for energy than health applications suggesting that any public calls for nano regulations may differ by technology sector. **[31]**

2. Nanosystems

2.1. Introduction to Nanosystems

The processes of modelling, design, and characterization apply the discoveries of basic scientific research to support the cycles of development that drive advances in technological capabilities. These processes are interwoven and mutually supportive. Modelling and design guide fabrication by providing a theoretical framework for generating and testing structures, devices, and entire systems by means of computational experiments. Modelling and design help choose targets for fabrication, and have proven to be valuable in areas as different as automobiles and molecules. The characterization of raw materials and complex systems provides data with which to assess not only the utility of a design, but the accuracy of models used to derive it. The iterative comparison of theory and experiment is important because many computational models of nanoscale systems (e.g., molecular mechanics and dynamics methods) are based on adjustable parameters, and the quality of the model and its results benefit from better experimental data. Thus, the characterization process, aided by continued advancements in imaging and measurement technologies, provides the data needed to validate or drive revision of both proposed designs and the underlying physical models that describe their properties and operation.

These can be assembled into molecules and various structure using various methods including directed self-assembly, templating, etc and may be positioned appropriately depending on the final requirements. Further along the devices architecture, integration, in situ processing may be employed culuminating in nanosystems, molecular devices, etc.

2.2. Transition from Nanotechnology to Nanomanufacturing

Throughout the world a huge amount of research is being carried out, and government and research organizations are spending large amounts of money and human resources into nanotechnology. This has generated interested scientific output and potential commercial applications, some of which have been translated into products produced on a large scale. However in order to realize commercial benefits far more lab-scale applications need to be commercialized, and for that to happen nanotechnology needs to enter the realm of nanomanufacturing. This involves using the technologies available to produce products on a large scale which is economically viable. Regardless of whether a top-down or bottom-up approach is used, a nanomanufacturing/nanofabrication technology should be:

- capable of producing components with nanometer precision;
- able to create systems from these components;
- able to produce many systems simultaneously;
- able to structure in three dimensions;
- cost-effective.

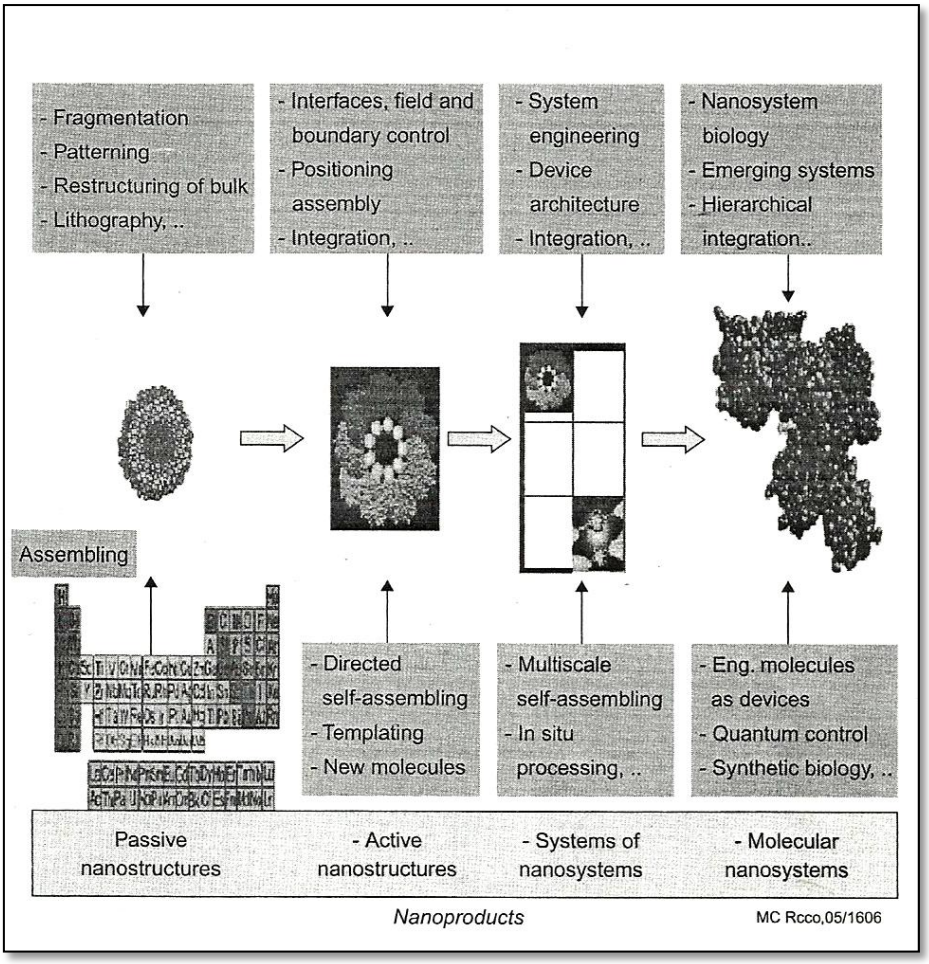


Figure-1.57.Summary of nanomanufacturing, shows the basic concept of nanomanufacturing[9]. Individual atoms, which are given in the periodic table, from the basis for nanomanufacturing

2.3. Productive Nanosystems

Atomically precise productive nanosystems are AP nanosystems that can be used to make any of a wide variety of structures under programmable control. Ribosome's and nucleic acid polymerases are examples found in nature. Metrics for productive nanosystems include:

• Block placement cycle time
• Error rate in placement
• Specific throughput (output rate per unit mass)
• Information content of products
• Metrics of the products themselves.

2.3.1. Major Subsystem Requirements

Productive nanosystems (present and projected) form a spectrum at least as broad as that of historical electronics, which has advanced from primitive crystal-diode radio receivers to teraflop computers. This spectrum can be divided roughly into early-, intermediate-, and advanced-generation systems. Anticipated early-generation systems of one class resemble

nanoscale systems found in biology today. After multiple intermediate technology generations, anticipated advanced-generation systems resemble automated factories with macro scale assembly systems fed with parts produced by macroscopic arrays of coordinated micro scale productive systems that are themselves based on nanoscale components. The subsystems required for these are, of course, radically different, and their requirements must not be confused. The paragraphs that follow consider some of the major functions that must be served in a productive nanosystem, and the kinds of subsystems required to implement them. In early-generation systems, the answer is often "nothing required."

2.3.1.1. System Architectures

The overall system architecture will depend on the technology generation of the APPN in question, and on its specific applications. Anticipated early-generation systems are of two basic kinds, although innovative ideas may broaden this conception. One kind, associated with tip-directed fabrication pathways, relies on mechanical conveyance and positional assembly to move parts; the other, associated with self assembly based fabrication pathways, relies on diffusion for this purpose. In either case, early-generation APPNs are anticipated to have little parallelism and correspondingly simple architectures. Anticipated advanced-generation systems are expected to converge on mechanical conveyance and positional assembly, which are favoured by considerations of reliability, control, efficiency, product scope, and so forth. Advantages of this approach are strongly indicated by exercises in design and modelling of different kinds of components and subsystems. It must be emphasized, however, that these prospective advantages in no way force early- or intermediate-generation systems to have these features, and they are in no sense requirements or defining criteria for productive nanosystems.

2.3.1.2. Control of Operating Environment

In early-generation systems, APPN mechanisms are expected to operate exposed to an ambient environment, which has its temperature and composition controlled by external means. The APPN itself requires no subsystem that performs this task. Paths through intermediate to advanced systems entail greater control of the environment, and at some point, transfer of more responsibility for that control to the APPN-based system. At the advanced end of the spectrum, control entails rigorous exclusion of unwanted molecules by barriers and control of transport through them. Only macro scale systems will require internal means for transport and rejection of waste heat; temperatures of nanoscale and micro scale systems will characteristically be closely coupled to the surrounding medium.

2.3.1.3. Feedstock Distribution

In early-generation systems, APPN mechanisms are expected to work with feedstock molecules transported for capture (by a tool-tip or a deprotected reaction site) by diffusion from the ambient environment (a gas or liquid). The APPN itself requires no internal subsystem that performs a distribution task. Local capture mechanisms suffice. Paths through intermediate to advanced systems entail increasing the control of feedstock distribution, as a requirement both of tighter control of operating environments and of the objectives of greater speed, reliability, and diversity of fabrication operations. This entails capture and subsequent transport. Separation of these functions can buffer internal mechanisms from statistical fluctuations in the timing of feedstock molecule capture. In macro scale APPN-based

systems, as in conventional macro scale factories, the paths and control of transportation can become complex.

2.3.1.4. Power distribution

In early-generation, ribosome-class systems, "power distribution" is a consequence of the delivery of chemical free energy together with feedstock molecules (which may be in bound forms). No internal "power distribution system" is required. Local energy coupling mechanisms suffice. Along paths through intermediate to advanced systems (and perhaps in early-generation systems on tip-directed fabrication paths), energy sources will perform multiple functions, requiring some form of power distribution. Along the path to advanced-generation systems, these subsystems again become complex, requiring transport over macroscopic distances and distribution to a large array of productive mechanisms. Electrical power distribution has been examined and appears adequate. Energy in chemical form is a natural alternative choice.

2.3.1.5. Information distribution

In early-generation systems with a single point of activity, the problem reduces to one of external distribution of information to the devices themselves, which can be accomplished by Any of several means (e.g., information molecules like nucleic acids, or modulation of light, pressure, or electric fields). No internal distribution of control information is necessary, because an external "broadcast" mechanism will suffice. Again, advances lead to a requirement for more internal structure. At some point, multiple devices must perform different, simultaneous operations at different locations. This entails a communication network subsystem, and can benefit greatly from the use of locally stored instruction sequences, and even computation. Mechanical or electrical means appear adequate for information distribution in practical systems. There is the opportunity to use the same distribution channel for delivery of both information and power. For instance the information can be encoded as a modulation of the power delivered to the individual units. The requirements on the information distribution subsystem will be strongly determined by the system architecture and complexity, and the system-level problems are of kinds familiar to manufacturing engineers and to programmers of parallel-processing computers.

2.3.1.6. Handling Finished Products

In solution-phase, early-generation systems, a natural approach is to simply release products that are themselves designed for self-assembly (or for "folding" of a chain of linked blocks). This avoids any requirement for a subsystem that handles products. Along paths through intermediate to advanced systems (and perhaps in early-generation systems on tip-directed fabrication paths), product handling requires transportation, and in larger systems, the transportation network can become complex. Anticipated macro scale APPN-based manufacturing systems employ micro scale transport systems to bring small blocks together to make larger blocks, as part of a hierarchical process that results in the assembly of macro scale products from parts of substantial size. The required architectures again involve problems of kinds familiar to manufacturing engineers and to programmers of parallel-processing computers.

2.3.2. Natural Productive Nanosystems

Biological productive nanosystems include:

• Ribosome's, which convert information in RNA into proteins
• RNA polymerase, which translates DNA into RNA
• Reverse transcriptase, which translates RNA into DNA
• DNA polymerase, which copies DNA to DNA
• RNA dependent RNA polymerase, which copies RNA to RNA

Some metrics that describe the operation of ribosome's are:

• Placement frequency $20s^{-1}$
• Error rate 10^{-5} to 10^{-4}
• Specific productivity ~10^{-3} s^{-1} (this is the reciprocal of the time required for the system to produce a mass of product equal to the mass of the system itself).
• Block size 110 Daltons
• Metrics for products—maximum size ~105 Daltons; Young's modulus ~109 N/m2; information content ~4 Kbits; maximum temperature ~100°C.

2.4. Systems for Application Areas

The following sections discuss several potential areas of application for AP nanosystems, some at the product level, some at the subsystem level, and of clear utility for products. In general, applications have the potential to expand greatly from early-generation products (sharply restricted materials, scale, and complexity; high cost) to progressively more advanced products (with materials expanding well beyond the familiar range, scale eventually growing to macroscopic, complexity limited by design capabilities, and costs potentially quite low).

2.4.1. Information Processing Systems

Add-Ones to Advanced Semiconductor Systems:-Semiconductor systems are increasingly limited by the Poisson statistics of implanted impurity ions that control the electronic properties of the transistors in the system. APM would provide a number of options to solve this problem:

• Atomically precise synthesis of electrically conventional transistors, but with atomically precise positioning of impurity atoms.
• Atomically precise synthesis of exotic, but proven, active devices, such as carbon nanotube transistors. A possible alternative is the use of planar graphene as the semiconductor.
• Atomically precise synthesis of devices which have gain, but which are not directly analogous to transistors. An example is a molecular tunnel diode with negative differential resistance. In addition to forming the active devices, integrating them into an otherwise conventional semiconductor fabrication process would require forming electrical contacts to conventional electrical conductors. Considerable work has been done on the interfaces between molecular electronics and conventional metals, as reported by Reed and associates **[50]** Replacing atomically imprecise transistors with atomically precise FETS throughout a system requires moderately high productivity from APM. An earlier hybrid application area

is in instrumentation, where the bulk of a system might be built by conventional techniques yet the critical sensor(s) would be built by atomically precise approaches. Patterned ALE would provide a very natural match to the substrates of modern,
But atomically imprecise, electronic systems for this type of hybrid system. Another type of hybrid of conventional microelectronics and patterned ALE might take place when the AP component of the system is capable of useful function (e.g., as STM tips) but is not yet capable of implementing logic or memory. Given some error rate in the patterning, it might be necessary to, for example, disable the non-functional STM tips, and the conventional FETS on the substrate might be used to do that.

2.4.1.1. Full Computational Systems

Given advanced atomically precise manufacturing, the devices described above continue to be available, and the atomic precision can be extended to the conductors in the design and to their interfaces with the active devices. In addition, the freedom to explore configurations other than active devices on a silicon surface allows more options devices, 3D organization, integrated cooling, etc.

2.4.1.2. Information-Oriented Optical Systems

For some applications, advanced APM systems will enable construction of better devices than we currently have for electronic-to-optical, optical-to-electronic, and nonlinear optical operations. In the specific case of nonlinear optical operations, second-harmonic crystals must have no centre of symmetry, but symmetry is difficult to avoid in conventional materials fabrication. The same molecular level asymmetry that produces the nonlinear optical feature tends to force crystallization in cells which oppose molecular dipole moments, and tend to cancel nonlinear optical effects. Productive nanosystems could by pass this limitation. For information processing, the gains likely in the optical domain are smaller than in some other domains simply because the scale of useful devices is set by the wavelength of light. The chemical flexibility of APM promises better materials, and the general manufacturing flexibility of APM promises easier integration of systems than current manufacturing allows, but this area presents fewer opportunities for strikingly new features than some of the other areas considered.

2.4.2. Medical Systems

Medical applications offer a broad scope for near-term, atomically precise systems. Several of these involve combing antibodies with labels or bioactive elements. For example, researchers have combined a magnetic moiety visible on NMR with a radioisotope and a near-IR fluorescent probe, all linked to antibodies that highlight different types of diseased tissues. **[48]** This is a covalently linked system with multiple functional pieces. The general availability of NMR as a position-sensitive readout mechanism (with many parallel channels at many separable chemical shifts) and the ability of in-vivo atomically precise systems to respond to many clinically interesting chemical parameters with a change in the NMR signal suggests that this is a rich area for near term applications. The nanoscale near-term opportunities in the medical area are related to therapeutics, principally in delivery systems, as described by Dr. Chiming Wei (see Wei, Paper 29, Working Group Proceedings): “In drug therapy, nanotechnology can dramatically improve the therapeutic potential of many water-insoluble and unstable drugs either through size reduction or encapsulation of the drug particles. In gene therapy, polymers and lipids can condense DNA into nanoparticles that can

be internalized by cells, followed by delivery of the DNA into the nucleus." While these examples are not atomically precise, Dr. Wei also cites dendrimers as attractive delivery mechanisms, and these are atomically precise. A wide variety of diagnostic applications of nanoscale technology are also cited by Dr. Wei:

• The use of semiconductor nanoparticles, quantum dots, as fluorophores which are far more resistant to photo bleaching than their organic dyes predecessors. "This increased photo stability is especially useful for three-dimensional (3D) optical sectioning, where a major issue is bleaching of fluorophores during acquisition of successive z-sections, which compromises the correct reconstruction of 3D structures."
• The use of scanning near-field optical microscopy (SNOM) to image cell ultra structure with much less perturbation of the cell than AFM imposes.
• The integration of atomically precise binding sites for a variety of potential anal ate molecules with nanowires to translate the chemical binding event into a change in electrical conductivity of the nanowire.
• Targeted contrast agents—"Techniques have been developed recently to achieve molecular and cellular imaging with most imaging modalities, including nuclear, optical, ultrasound, and magnetic resonance imaging (MRI)." Over the longer term, APM and medical applications are a natural fit. Living materials are intricately structured on the nanoscale. Many interactions between our cells involve complex nanoscale actions (e.g., the presentation of antigens in [what is the name of the cells involved?] out immune system). It seems reasonable to expect both diagnostic and therapeutic activities to involve more and more materials structured on this scale. With very advanced APM, the potential exists to construct systems that are substantially better than the biological subsystems in healthy humans. For example, there have been theoretical studies of micron scale AP systems ("respirocytes") that would perform the same oxygen transport task as erythrocytes, but with an oxygen-carrying capability greater by 2 orders of magnitude.

2.4.3. Energy Conversion Systems

Generally speaking, APM has the largest impact on energy conversion systems where throughput is directly affected by the nanoscale or atomic scale features of energy conversion components. For example, theoretical studies of advanced-generation AP electrical motors have yielded designs with power densities >1012 W/m3, far above current capabilities, yet chiefly a consequence of elementary mechanical and electromagnetic scaling laws. Bulk power conversion is not a clear near term target for APM. The current costs of AP fabrication from both self-assembled and scanning probe approaches are too high to be competitive in bulk energy conversion, though specialized niche applications may still find them useful. With plausible cost reductions and performance advantages, however, systems incorporating AP self-assembled structures may prove attractive in this area, and this potential is well worth exploring. Nonetheless, considerable attention has been given to solar power applications of nanoscale component technologies, both photovoltaic and photochemical. **Photovoltaic**. For comparison, note that existing silicon photovoltaic cells can reach an efficiency of 24% (at 0 C) **[51].** The limitations on the cells include rigidity/fragility, degradation over time, and the high cost of fabrication. Near term nanoscale technology offers options such as organic photovoltaic's, with lower costs, better flexibility, but with reduced efficiency (~5%).

Photochemical Near term nanoscale approaches (albeit atomically imprecise) have yielded significant results (11% efficiency) **[49].**

Electrochemical/Fuel Cells/Batteries From a systems perspective, the ability to, for example, integrate transportation of solid fuels and fuel cells on a sub-millimetre scale would permit many products that would be infeasible today. For instance, it would become feasible to feed a solid graphite crystal into a fuel cell, with atomically precise coordination between the fuel feed and the electrode reactions. In the shorter term, the molecular-scale nature of the key physical processes in batteries and fuel cells has already attracted extensive research in nanostructure materials. AP nanostructures hold great promise in this area.

2.5. Characterization Background

Improvements in characterization and in the computational resources vital to modelling and design have greatly advanced developments in the scientific disciplines that provide the foundations for nanoscience and nanotechnology. The available characterization methods span the range of familiar molecular study, from the investigation of bulk materials at the macro scale (refraction/reflection studies, stress and stiffness measurements, tribology), to the study of molecules in periodic systems (crystallography, electronic spectroscopy, vibrational spectroscopy), to the study of individual molecules at defined positions (atomic force microscopy, scanning tunnelling microscopy). As in modelling and design, the choice of characterization method is highly dependent on the desired property to be measured, and currently available techniques can far exceed the level of detail required for the characterization and testing of materials. Currently available techniques for the characterization of nanostructures are sometimes bottlenecks in development, but are adequate to support ongoing progress in AP nanosystems and APM: the complete characterization of atomic scale properties is not on the critical path. In self-assembled structures, the subunits are multi-atomic and are typically independently characterized. In many instances, knowledge of their relative positions in a larger structure immediately provides atomic-scale information based on the prior characterization of the subunits themselves. With the structure and properties of individual system components defined during their initial fabrication, characterization can focus on properties at the device and component levels.

2.6. Modelling and Design Background

Nanoscience and nanotechnology are on the verge of tremendous advances in modelling and design that originate in macro scale engineering, chemistry, and computer science. The modelling and design infrastructure that has developed around macro scale engineering, including computer aided design-based mechanical and electrical engineering, provides a solid foundation of protocols and design interfaces that are now being extended to software for molecular modelling and design. The fields of quantum chemistry, molecular dynamics simulation, and molecular visualization combine to provide the modelling and design tools that enable the study of matter at the atomic scale, from molecular orbital calculations of small molecules to the study of binding interactions between bio molecules, such as DNA and proteins that span well into the nanoscale regime. Nanoscale modelling and design merge macro scale engineering principles with quantum mechanical and classical mechanical models of matter, all the while driving demand for more data, more accurate models, faster algorithms, and improved computational resources. Just as modelling and design will set the pace of development for many atomically precise technologies, developments in computers and algorithms are driving the extension of atomistic models, the modern basis for our understanding of matter, into the nanoscale regime. The validity of a design and the predictive power of a theory-driven design process are heavily dependent on the accuracy of

the theoretical model(s) being used. The choice of quantum mechanical, classical mechanical, or hybrid descriptions for the study of molecular and nanoscale systems is one determined by both theoretical necessity and available resources. While quantum mechanical methods exist that can approach the absolute limits of accuracy achievable by modern computational chemistry, the use of these methods is currently limited to diminutive chemical systems (< 20 atoms) because of computational cost. The selection of a quantum mechanical or classical mechanical description of a system is one driven, within the limits of available resources, by the properties being considered, with decades of both molecular mechanics and quantum chemical developments available from which a researcher can consider a system for their properties. The difference between modelling and design for the study of both chemical and nanoscale systems is clear: while the field of molecular modelling is one that has readily accepted a formal division between quantum and classical methods for the study of materials, the field of design is not naturally subject to that constraint. While molecular modelling studies occur within the limitations of each theoretical method, the goal of nanoscale design is to produce the best structures or systems possible according to a set of value metrics, making the use of multiple modelling approaches (because of their known limitations) an integral part of the design process.

2.6.1. Atomically Precise Technologies Span the Range of Available Modelling Techniques

The modelling and simulation of materials, devices, and systems within the nanoscale regime (1 to 100 nm) requires atomistic or near-atomistic ("reduced model") methods. In systems that are designed to perform chemical or mechanosynthetic operations, processes involving fundamental changes to the electronic structure of materials, the modelling and design process requires quantum chemical methods or "reactive potential" methods, empirical approaches that include as part of their parameterization process terms that account for the relative energies of chemical bonds. In systems or assemblies that do not undergo chemical reactions but instead maintain fixed atomic connectivity in the course of a series of operations, classical mechanical approaches have proven to be effective. Nowhere has this division in modelling techniques been more relevant to the study of structure and function in nanoscale systems than in the modelling of the enzymatic (quantum mechanical) and conformational (classical mechanical) properties of proteins. While the broad range of molecular modelling techniques enable the complete atomistic representation of matter across the nanoscale, the application of many techniques is limited by computational resources. Computational chemistry must balance the advantages of accurate theoretical models to describe the properties of atoms and molecules against the limitations of available computational resources. Molecular mechanics and semi-empirical quantum chemical methods have far lower computational demands than rigorous ab initio methods and density functional theory. Their formulation is largely pragmatic, implemented for the interpretation, then prediction, of chemical data during the decades when room-sized computers had a fraction of the power of the most modest personal computers today. Improvements in resources and algorithms to reduce the computational cost of calculations have made all theoretical tools more available, yet the most exact methods are barely capable of property prediction in the nanoscale regime due to the cost of computation. Thousand-atom classical dynamics simulations and ten-atom ab initio calculations tested the limits of computational resources at the beginning of the personal computer revolution, yet today, entire nanoscale devices and complex biological systems (>106 atoms) can be simulated by classical mechanics methods, while hundred-atom systems can be readily treated by ab initio methods and density functional theory on computer clusters employing commodity hardware.

Developments in computing power and algorithms have pushed the tools of computational chemistry into the nanoscale regime, with each new generation of processor extending the speed, scale, and accuracy of calculations.

2.6.2. Atomically Precise Technology Design Requires Multi-Level, Multi-Scale Modelling

By their nature, atomically precise technologies and their operations require atomistic models. The dependence of the properties on atomistic structure is particularly important when considering structures whose dimensions are in the nanoscale (1 to 100 nm) regime, as the atomic building blocks of these objects are within only two orders of magnitude of the size of the structures themselves. Beyond this, however, domain-specific requirements, including quantum mechanical, atomistic classical mechanical, and "reduced model" approaches, vary widely. Processes that involve bond rearrangement, unusual structures, electron transport, or electronic state transitions typically demand quantum-mechanical modelling of electron distributions and energies. Processes that involve atomic motion, molecular displacement and deformation, or any types of structural analyses that preserve the atomic connectivity of the system under investigation are typically addressed by molecular mechanics and molecular dynamics methods. To reduce computational burdens in chemically massive structures that do not require consideration of all atoms, reduced models are common, treating groups of atoms as single bodies, or (in the limiting case) subsuming them into non-atomistic models of elastic or even rigid solid bodies. At this level, the techniques are those familiar to macro scale modelling and design. Choosing a specific model always involves trade-offs of the speed of computation, the size or amount of structures modelled, and the required accuracy of the results. Quantum methods in particular embrace a range of models (levels of theory) that differ widely in their computational tractability: some allow dynamical studies of thousands of atoms; others strain available computational resources in order to provide great precision in describing small molecules. Molecular mechanics and dynamics models rely on direct approximations to the forces among atoms, and currently scale to systems with up to millions of atoms. The accuracy of the latter methods (for suitably chosen classes of systems) can be judged by the fact that they are used to gain insights into the balance of weak interatomic forces responsible for the geometry and dynamics of proteins and other bio molecules. The development of combined quantum mechanical and molecular mechanics methods for the study of chemical systems (QM/MM methods) is founded in the realization that the local changes to electronic structure (bond breaking, formation) in macromolecules or molecular aggregates can be dependent on the larger system. This is readily apparent in the simulation of protein function, where enzymatic activity is confined to a specific location but the geometry and dynamics of that location are a function of the protein structure as a whole. The further reduction of atomic detail, through the use of subsumed detail/rigid body models for molecules or continuum models (such as implicit solvent models and non-atomistic surface models) enable the removal of a further level of detail that would otherwise require tremendous increases in atom count and, therefore, computational cost. Extending the scale, scope, and accuracy of atomistic modelling techniques is a high priority and can greatly facilitate atomically precise technology design and implementation. Integrating atomistic and nonatomistic models at different scales is key to enabling practical design and simulation of large, complex atomically precise nanosystems. This is an area of ongoing research activity, driven by areas related to, but developed in parallel with, nanotechnology, including biochemistry, supramolecular chemistry, and materials science.

2.6.3. Atomically Precise Technology Developments Demand Innovations in Computer-Aided Design

Design and molecular modelling are, at their cores, indirect tools for the prediction of chemical properties and phenomena. The process of design at the atomic level connotes the application of models, be they physical or mathematical, for the generation of new structures with desired properties. As such, design and molecular modelling are formally distinct areas within theoretical chemistry that have evolved towards tight integration, with design now commonly a process of the application of the predictive powers of the computational methods within molecular modelling for the in silico generation and testing of structures or whole systems. The design process for molecules and nanosystems exploits physical descriptions based on diverse molecular modelling and continuum model techniques, with the results and Interpretation of generated data subject to their approximations and computational restrictions. The utility of design at the nanoscale depends on the adequacy of the theoretical model(s) used to describe the physical system. In many instances, potential designs can be tested and modified at timescales and expenses far below those of physical experiments. These modelling and design exercises can be of great value provided that they are accurate enough to provide guidance that yields even moderate improvements in the success rate of the more expensive physical experiments. Accordingly, even highly imperfect models can play a valuable role. Each domain of atomistic modelling (e.g., quantum mechanical, atomistic classical mechanical, reduced model methods) creates distinct demands on computer aided design (CAD) tools. Some of these demands involve data visualization, while others involve data representation, and its integration with methods employed in subsequent analyses that may or may not be atomistic in nature. (Examples include the study of electrostatic interfaces or molecular lock-and-key binding, both of which can employ surface analyses based on previous calculations of atomic positions). At all but the largest scales, conventional approaches to design are inapplicable because of the discrete nature of component structures: one must drop the assumption that dimensions, electrical properties, etc., can be varied in a continuous way. This is in many ways more fundamental than differences in the applicable device physics. Multi-level modelling is motivated by the great differences in scope and computational cost associated with different modelling techniques, and this will need to be integrated into CAD tools and the design process in two distinct ways. The first is the application of different techniques to different parts of systems, for example, applying quantum methods to describe reactions, while applying molecular mechanics methods to describe the structures that support and constrain the reacting components. This has been achieved, for example, in modelling structure/ property/function relationships in enzymes. Expanding this principle to mixed models of more kinds is an important objective. The second role for multi-level modelling is design refinement. In this application, less accurate, lower-cost techniques are used for exploratory purposes to identify systems that are worth further investigation using more accurate, higher-cost techniques, a process that maximizes throughput of designs by leveraging the speed of computation with a prior knowledge of the limitations of the employed models. It will be important to provide smooth integration of this methodology into CAD tools for developing atomically precise technology systems.

2.6.4. Characterization Methods Enable Refinement of Models, Designs, and Fabrication Methods

The development cycle in systems engineering proceeds through modelling and design (for example, computational simulation) iterations until an apparently satisfactory result is achieved. Fabrication and physical testing then provide the ultimate feedback on the success of a design. The quality of this feedback determines its effectiveness in guiding any necessary revisions in the fabrication method, the model, or the design. It is crucial to know, for example, whether a failure results from a difference between what was designed and what was made (a fabrication problem), or from a difference between the properties predicted and the properties observed (a modelling problem). In nanoscale modelling and design processes that employ the quantum and classical mechanical tools of computational chemistry, issues based on modelling accuracy are either straightforward (classical mechanics) or difficult (quantum mechanical) to overcome. As an entirely empirical class of tools, classical mechanical models of atomic motion are readily capable of being refined based on the results of experimental observation, subject to either the modification of the underlying parameters or to the increase in computational resources required to accommodate additions to the force field model used to define all atomic interactions. The same is not true of ab initio methods or density functional theory. In the case of ab initio methods, the benefits and limitations of Hartree-Fock and post-Hartree-Fock (MPn, CI, CC, CASSCF, etc.) methods are inherent to the mathematical approximations used to describe the quantum nature of chemical systems. For density functional theory, where the density functional used to model the static correlation of electrons are empirically derived, the procedure of density functional optimization is far from trivial because, unlike the nearest-neighbour(s) parameter-based molecular mechanics methods, changes to density functional are not limited to local changes in structure. Within each quantum chemical theoretical model, improvements to ab initio and density functional theory calculations largely come through improvements in the description of electronic wave functions, made possible by the selection of larger and more computationally demanding basis sets. Improved characterization methods generally will aid in the development of atomically precise nanosystems, but the needs and ingenuity of the scientific community have already provided remarkably capable tools that can help to refine those computational models that use experimental data in of their parameterization process. Nanoscale and atomic-scale sensing, imaging, and metrology have immense capabilities and are growing rapidly. Improved tools for characterizing atomically precise nanosystems will be of great value, but the present state of the art provides an adequate basis for progress.

2.6.5. Advances in Atomically Precise Fabrication Technologies Can Simplify Modelling Requirements

Advances in atomically precise fabrication will enable practical applications of an increasing range of structures and phenomena even beyond the nanoscale. This will, in turn, increase demands on modelling techniques by driving expansion of their scope and increasing the demand for faster and more routine methods that are applicable in the context of nanosystem design. In one important respect, advances in atomically precise fabrication can make successful modelling less demanding by reducing the design space that must be modelled to test proposed systems. Advanced fabrication techniques can, in many instances, make components with improved stability, rigidity, and performance. These improvements tend to make the structural behaviour of components less sensitive to small errors in model energies, and they can also be used to increase the margin of safety by which components satisfy

design requirements. This again reduces sensitivity to errors. Constraints within the fabrication process can also be included in the modelling process and used to, for instance, remove possible degrees of freedom from a simulation. Such simplifications are difficult to incorporate into chemical simulations, where the system is inherently chaotic, but are readily included in mechanosynthetic, epitaxial, or various programmable processes at the nanoscale, where systems can be constrained to operate in a more controlled manner. As a consequence, currently accessible products of AP fabrication may require more advanced modelling techniques, while analogous advanced products may not. This inverse relationship is illustrated by molecular machine systems, where protein-based devices remain a great challenge to modelling, but not to fabrication, while machines made of rigid atomically precise components can be easy to model despite being inaccessible to current and near-term fabrication techniques. This relationship facilitates, to an unexpected degree, the use of current modelling techniques to explore and evaluate the general properties of classes of systems in order to weigh their potential value as longer-term development objectives.

2.6.6. Atomically Precise Technology Development Can Succeed Despite Deficiencies in Modelling Techniques

In assessing the near-term potential for the design and fabrication of atomically precise systems, it is necessary to assess the adequacy of existing modelling techniques for supporting the design process. This is a matter of particular concern because there exist many physical systems of interest for which the predictive power of existing tools capable of modelling structures and properties at nanoscale dimensions is very poor, often giving qualitatively incorrect results. For instance, many quantum chemical methods are inadequate for predicting bond dissociation energies, electronic transition energies, or the association of weakly interacting molecules or structural motifs. Molecular mechanics methods are extremely susceptible to errors in atomic geometry and connectivity in the absence of algorithms to confirm the chemical accuracy of starting structures, a limitation that affects both the accuracy of calculations and the usability of such methods by untrained users across nanoscience disciplines. For design problems, the adequacy of a model cannot be assessed without considering the practical question it must answer. Design can succeed, and even be reliable, in domains where models have substantial inaccuracy and can give qualitatively incorrect results. What is required for success is not universal predictive accuracy, but instead the ability to identify a suitable class of systems within the domain. To be suitable for the purpose of design, members of this class must be sufficiently well-behaved to be insensitive to modelling errors, and the class must include members that satisfy the relevant set of design requirements. What constitutes sufficient insensitivity, however, typically depends on whether these requirements are stringent or loose, hence the importance of knowing the practical design question before judging the adequacy of a model. Even a very incomplete knowledge can aid a technology development program. Even a weakly predictive model can speed development by directing experimental research away from likely failures and toward Systems that are viable candidates for success. While the Edisonian efforts of experimental trial and error alone can be an acceptable development method (provided that success is sufficiently common and that trials are not prohibitively slow or expensive), model-based approaches even with limited tools provide a level of rational design that can aid in the application of experimental precedent and chemical intuition.

2.7. Design Considerations for Self-Assembled and Directly Assembled Nanostructures

The availability of both self-assembly and directed (mechanical, programmable) approaches at the nanoscale for the generation of new materials or complex systems provides both considerable flexibility in possible fabrication routes and considerable challenges for computational modelling and design techniques. For structures to be made by means of tip-directed atomically precise mechanical processes, product geometry results directly from a programmed sequence of motions of a tool with respect to a workspace. This directness applies both to current and next-generation atomically precise technologies based on scanning probe instruments and to envisioned advanced-generation productive nanosystems. Domain specific CAD requirements in this area are driven chiefly by the need to model discrete structures with appropriate device and process physics. In atomically precise self-assembled systems, by contrast, structure and fabrication become related in a far more intimate way. At every stage of assembly, at least one component must be free to diffuse in a solvent, enabling it to explore all possible positions and orientations to find its unique, intended binding site. This process requires that the component be soluble, that it has a surface complementary to that of its intended binding site, and that all other surfaces of the workspace and the component be sufficiently non-complementary that stable binding is precluded. These requirements are added on top of functional requirements. The available materials and environmental conditions in nature favoured complex structure generation by way of self-assembly methods, a general process that has been exploited with tremendous success in the field of supramolecular chemistry and, increasingly, the control of molecular crystallization. Identification of designs in which components have appropriate surfaces and matching interfaces characteristically requires an automated computation search mechanism. In many DNA structures, "sticky ends" serve as complementary interfaces, while in proteins; folding requirements can be viewed as extending self-assembly constraints to the interior of the molecule. In both instances, design tools today rely on searches in the combinatorial space of alternative monomer sequences. Improving success rates and product performance will likely require improvements in this class of algorithms, chiefly in the definition of suitable objective functions. Such tools will also serve useful roles in the design of much larger nanoscale systems based on self-assembled components, where complementary surface interactions can be combined with control of the sequence of assembly. With In atomically precise self-assembled systems, by contrast, structure and fabrication become related in a far more intimate way. At every stage of assembly, at least one component must be free to diffuse in a solvent, enabling it to explore all possible positions and orientations to find its unique, intended binding site. This process requires that the component be soluble, that it has a surface complementary to that of its intended binding site, and that all other surfaces of the workspace and the component be sufficiently non-complementary that stable binding is precluded. These requirements are added on top of functional requirements. The available materials and environmental conditions in nature favoured complex structure generation by way of self-assembly methods, a general process that has been exploited with tremendous success in the field of supramolecular chemistry and, increasingly, the control of molecular crystallization. Identification of designs in which components have appropriate surfaces and matching interfaces characteristically requires an automated computation search mechanism. In many DNA structures, "sticky ends" serve as complementary interfaces, while in proteins; folding requirements can be viewed as extending self-assembly constraints to the interior of the molecule. In both instances, design tools today rely on searches in the combinatorial space of alternative monomer sequences. Improving success rates and product performance will likely require improvements in this class of algorithms, chiefly in the definition of

suitable objective functions. Such tools will also serve useful roles in the design of much larger nanoscale systems based on self-assembled components, where complementary surface interactions can be combined with control of the sequence of assembly. With suitable nanomechanical systems, blocks with complementary surface interactions could be guided to the region where they are to bind, relying on complementarily to select a precise position and orientation within the looser, and imposed constraint. By analogy with Lehn's concept of "supramolecular chemistry", in which chemists exploit non-covalent binding interactions, this might be termed "supramolecular mechanosynthesis". Future-generation atomically precise self-assembled systems, perhaps exploiting components produced by new classes of atomically precise productive nanosystems, appear likely to share this requirement for integrating search-based operations in CAD tools and design processes. A similar need for searches will arise when tip-based atomically precise mechanical systems are used to manufacture structures that satisfy surface-defined constraints by means of structures that depart greatly from crystalline order.

2.7.1. Modelling Challenges at the Nanoscale

Modelling and design at the nanoscale is on a leading edge of developments in computational chemistry, pushing research in algorithms, visualization, and theoretical models. Nanostructures and nanoscale devices often challenge our ability to study matter by atomistic (both classical and quantum chemical) methods. Nanoscale modelling and design, like nanoscale materials and devices themselves, often straddle classical and quantum mechanical descriptions. Large-scale models may straddle the boundary between atomistic and continuum models, where the latter are adopted because of their great computational economy. The use of classical atomistic or even continuum approximations for modelling and design is largely pragmatic, founded in computational necessity. The cost in computational resources to handle even moderately-sized molecular systems using quantum mechanical descriptions is beyond what even the largest computational facilities can provide. The challenges of large, atomistic models can be enormous even in classical approximations, as shown by the scale of resources applied in the supercomputer and distributed computing studies of the protein fold-prediction problem.

2.7.2. Molecular Graphics Developments and the Visualization of Nanoscale Structures and Information

The visualization of chemical information is as important to the researcher as the underlying physics is to the validity of the model. Advances in molecular graphics, like advances in the scales of molecular modelling, have a long history of expansion and improvement as a result of advances in general computational technology. While the visualization of molecules and their interactions by way of graphical molecular modelling programs have greatly aided the experimentalist in chemical research by diminishing the conceptual barriers to theoretical methods, the same graphical implementations have also aided theoreticians by providing a rapid means to identifying errors in models that can result from fundamental limitations in the theoretical methods themselves. An important aspect of molecular graphics relevant to nanoscale design and simulation concerns the relevance of atomistic representations of chemical information. Considerable information can be obtained from non-atomistic visualizations, for example, of the DNA helix and base pairing. This reduction in model complexity extends to all areas of visualization, where the properties deemed relevant to a single calculation or simulation can be defined purely by the shape of a molecule and not its

atomic constituents. Many properties important to nanoscale design, such as charge distribution, dipole moment, molecular volume, and surface geometry, need not be defined with respect to individual atoms. In the case of surface renderings for the identification of binding regions, possible interfaces for assembly, or the determination of molecular volumes, suppression of atomistic detail can provide a more useful display of the important physical properties. Again, computational biochemistry provides excellent examples: the reduction of protein to secondary structure (ribbons and geometric objects for representing alpha helix and beta sheet motifs) or surface renderings (charge analyses, binding pocket visualization) has been vital both for understanding structure and function and for presenting this information to other researchers. Similar representational strategies will be widely applicable in the design and evaluation of AP nanosystems.

2.7.3. Smart Design Methodologies and Issues Related to Model-Based Chemical Knowledge

The visualization of molecular information has driven both open source and commercial software development that has broadly expanded the utility of molecular modelling programs to researchers that need not be familiar with the underlying theory to apply the methodologies to chemical design. The advantages and limitations of molecular modelling techniques extend into the design process, with atomistic design processes subject to both constraints imposed by the modelling limitations and an absence of "chemical knowledge" on the part of graphical programs. Simply, atom-derived properties, such as chemical reactivity and stability, are not readily accounted for within molecular design and CAD systems, leaving proposed designs subject to critical evaluation by researchers even with exhaustive computational studies completed at high levels of theory. A major obstacle to accurate atomistic design within the nanoscience community as a whole is also to be found in the incomplete incorporation of chemical bonding and atomic geometry information in visual molecular modelling packages. This aspect of visual molecular modelling packages has less to do with limitations of the molecular modelling methods available in the program and more to do with the chemical knowledge of the user. Any effort to greatly expand the usability of computational modelling and design systems for nanofabrication must include, as part of its functionality, the ability to identify, if not correct, flaws in atomic connectivity and geometries from "standard models," both for those users unfamiliar with the complexities of chemical bonding (a likely situation as the tools of interdisciplinary research become available in advance of knowledgeable users) and for chemists and biologists fully knowledgeable in chemical bonding but unable to readily visualize problematic locations in chemical structures due to the shear size of the structures being designed. In the absence of intelligent systems capable of comparing calculated geometries against databases of all known molecular motifs or theoretical models of atomic geometry and chemical bonding, the final validation of any design still lies with the researcher. The extent to which chemical knowledge can be programmed, or rules governing chemical bonding and non-covalent interactions can be developed to obviate the need for intensive pre- and post-processing by researchers, into a graphical design system to simplify nanoscale design is an important area of future study that extends from molecular modelling packages, themselves still developing such functionality.

2.8. Modelling of Nanosystems

The predictive modelling of mechanical and electronic phenomena in the 1 to 100 nm range is being extended through improvements both in computational algorithms and computer technology. The rapid improvements in processor performance have driven theoretical work in all fields of science and are well known. However, while processor performance alone could drive the extension of theoretical studies to new size regimes, the development of efficient, scalable software has also had tremendous impact on the field of molecular modelling by enabling independent researchers to use commodity hardware in individual laboratories to approach the computational speeds of dedicated supercomputers. Nanoscale science presents new challenges to both experimentalists and theoreticians. While experimentalists are exploring novel properties of materials at this scale, theoreticians are exploiting computational resources powerful enough to study nanoscale systems using molecular modelling tools developed for small systems in computational chemistry. Theory and computation become useful in an area of science when their predictions become reliable enough to help improve the success rate of experiments, and they become essential to an area of technology design when their accuracy is sufficient to guide the selection of system-level implementation targets. The balance of theoretical accuracy and computational cost frequently motivates molecular researchers to perform survey-style studies of model systems using lower-quality computational methods, followed by final studies of candidate systems by high-level methods. The growth in computational resources has made this approach less important for structures of the sort to which it had been applied, but extension of molecular modelling approaches into the nanoscale reintroduces the benefits and limitations of low-accuracy models as a screening mechanism for design, and as a guide to the requirements for applying more accurate and expensive methods. Models with substantial inaccuracies and limited applicability can nonetheless provide effective tools for system-level design in suitably selected domains. There are several reasons for this:

• System-level designs can in some instances be restricted to employ only relatively well-understood components (consider the role of DNA oligomers in structural DNA nanotechnology).

• Designs may incorporate margins of safety, making them insensitive to small errors in predicted geometry or energy.

• A system-level design may permit many alternative component-level implementation options, and modelling may strongly suggest that one or more will work, yet not specify which. This is a particularly important realization regarding the relationship between nanosciences in general and the emerging technologies of nanosystems engineering.

2.8.1. Computational Infrastructure

Efforts in computational nanoscience span the range of resources and facilities, from individual researchers performing computational studies at academic institutions to major national laboratory investigations and method development projects using (or designing) state-of-the-art computational resources. Further model refinements and improved computing resources will increase the reliance of researchers on theoretical methods for the design and testing of materials and complex devices. Providing researchers with computing resources powerful enough to address their questions with the highest or most appropriate levels of theory available has been addressed at the US national level through the establishment of the National Centre for Supercomputing Applications (NCSA), the support for major computational facilities at many of the national laboratories, and the provision of funding through many of the national agencies (such as NIH, NSF) for computational facilities at

individual universities. A benefit of concentrating resources at national facilities is the development of communities of computational chemists familiar with the many programs available for theoretical study and the knowledge of the strengths and limitations of various theoretical methods with respect to research projects proposed by applicants.

2.8.2. Information Provided by Molecular Modelling Methods

Within the field of molecular modelling are the mathematical foundations for the property calculation of any atomic assembly, including both static properties (geometry, potential energy surfaces) and dynamic properties (excitations, transition states, electron transport). Molecular mechanics/dynamics methods, while providing the least realistic descriptions of atomistic matter by their neglect of electronic structure, have proven instrumental in computational chemistry by enabling the study of macromolecules and their interactions, the dynamics of classes of molecules in their crystal cells, and the thermal transport properties of materials, to name only a few applications. The clearest division between the available methods in molecular modelling is between methods that provide electronic structure information and those that do not. This division separates classical and quantum mechanical descriptions of matter, a recurrent theme in much of the discussion of modelling and design. Neglecting computational demands, higher levels of theory are generally capable of calculating the properties of lower levels of theory. In the case of post-Hartree-Fock methods capable of predicting electronic transitions and excited state geometries, these same methods can also be used to calculate the ground state geometries of molecules to very high levels of accuracy. Quantum chemical methods not only can perform the same geometry and dynamics calculations as molecular mechanics methods, but provide the foundations for many molecular mechanics methods. These derive their force field parameters from ab initio and density functional theory calculations. A brief summary of some of the properties available from molecular modelling techniques are provided below. The division between classical and quantum mechanical methods, as well as quantum chemical methods suited for “static” (ground state) and “dynamic” (excited state, transition state) electronic processes, are used to divide the property prediction of the available techniques.

Non-Electronic Structure Property Prediction (Molecular Mechanics/Molecular Dynamics)

Ground state geometries, dynamical behaviour, conformational energies, self-assembly processes (such as protein folding and unfolding), electrostatic binding and repulsion energies, transport of thermal energy, molecular transport through materials, ligand binding geometries and positions, molecular volumes and surface areas, steric and electrostatic surface interactions, crystal dynamics and phonon energies, solvent-accessibility in macromolecules…

Static (Ground State) Electronic Structure Property Prediction (Hartree-Fock and post-HF Methods, Density Functional Theory)

(Including the above non-electronic properties) energies of reactants and products in chemical reactions, energies of alternative/side products, rigorous electrostatic dipoles and multipoles, energies and intensities of vibrational transitions (IR, Raman, neutron), nonlinear optical coefficients, solvent dependences on molecular properties, ionization energies, electron affinities, occupied molecular orbital energies (and approximate unoccupied orbital energies), chemical reaction heats of formation, rigorous electron density and charge

distributions (Mulliken, Lowdin, Hirshfeld, Bader, Weinhold, etc.), force constants/parameters for molecular force field calculations…

Dynamic (Excited State, Transition) Electronic Structure Property Prediction (Time-Dependent DFT, CC, CI, CASSCF, MCSCF)

(Including the above properties) energies of transition state barriers, transport of electrons/holes, electronic transition energies and spectral predictions, oscillator strengths of electronic transitions, spin-spin interaction dynamics, geometries and relative energies of transition states, modelling of catalytic pathways…

2.8.3. Molecular vs. Solid-State Molecular Modelling

The defining characteristic of molecular-based modelling, as it applies to nanoscale modelling, is that the environment within which the calculation is being performed is finite. Molecular based methods are concerned primarily with the "system" and not the "surroundings," although some variants on molecular theory can address how a molecule/system might behave in a medium (such as through solvent modelling or the application of external electric/magnetic fields). In single molecules or discrete clusters of interacting molecules, molecular-based methods provide a wealth of information, including the relative binding energies of intermolecular interactions. When the surroundings (such as solvent) do not interact appreciably with the system, molecular-based methods can provide excellent agreement with experiment. The isolated-molecule approximation breaks down when the system under study is bound within a periodic framework (such as a molecular crystal), as the system and surroundings are now one and the same. Solid-state theory, the application of periodic boundary conditions to include the surroundings within a calculation, is the "infinite" counterpart to molecular theory. Solid-state theory is the theory of materials, be it atomically-pure materials, mixed atomic lattices of insulating/conducting/semiconducting materials, amorphous solids, or molecular crystals. Solid-state theory provides means for studying the macroscopic properties of materials, such as those important to materials scientists and engineers. Solid-state methods have only recently reached the level of detail and accuracy of molecular methods through the introduction of density functional theoretical implementations of solid-state code and the availability of computational resources capable of performing the calculations. Periodic boundary conditions can now be employed for the study of crystalline materials, amorphous materials modelled with periodic boundary conditions in order to artificially impose environmental constraints in a more physically realistic manner (as opposed to the solvent shell methods of molecular quantum theory), and idealized structures that exploit the spatial restrictions of the periodic boundary conditions (such as by fixing the separations of interacting structures bound along lattice planes).

2.8.4. The Multiple Levels of Modelling and Design

Theory-driven design at the nanoscale is subject to the strengths and limitations of the many methods available in computational chemistry for the study of matter. It is important to understand the limitations of each level of theory due to their approximations, as some of these limitations make the theories wholly inadequate for answering some questions. The strengths, limitations, and some of the likely future directions of many molecular modelling methods are summarized in **Tables 1.3** through **Tables 1.3-1.7.**

Capabilities	Limitations	Projected Advances	Typical Applications	Projected Applications
Subsection: Molecular Mechanics — >10^6 Atoms				
Energy minimization and optimization of ground state geometries	Most force field development and available parameters are biased to biology	The continued generalization of force fields to many types of chemical systems	Molecular structure rectification prior to quantum chemical studies	Rapid prototyping of structural motifs and mechanical processes at the nanoscale
Molecular surface generation for electrostatic maps, binding geometries	Final structures and relative energies of conformations are only as accurate as the force field being used	Computational developments, algorithm developments to push these methods into the mesoscale regime	Binding and steric interaction studies for supramolecular complexes, biological molecules	Provides the computationally feasible basis for atomistic mesoscale representations
Subsection: Molecular Dynamics — >10^6 Atoms				
Simulation of molecular motion and the sampling of conformational space	Dynamics simulations and conformational energies are only as accurate as the force field being used	Continued extension to larger and systems (beyond a complete virus)	Rapid prototyping of small molecule designs	Studies of thermal stability of non-covalent structures
Bases for explicit solvent models, periodic boundary conditions (crystals), amorphous solids, and molecular aggregates	Absence of libraries of parameters for non-biological systems means some systems cannot be studied or are treated using approximate parameters	Scaling methods and analyses to extend over various chemically relevant time scales (vibrations to protein folding); multiscale modeling integration	Thermal, vibrational, steric, and structural studies of molecules, intermolecular interactions and macromolecules	With QM/MM implementations, modeling of covalent bond assembly processes in macromolecular, nanoscale systems
Linear scaling of bonded interactions, quadratic scaling of non-bonding interactions	Inorganic clusters, solid-state species are insufficiently accounted for in most current implementations	Environmental dependence of transition state geometries with quantum mechanical integration	Simulation of molecular/ion transport mechanisms within macromolecules	Simulations of transport phenomena in nanofabrication processes
Structural accuracy achievable through parameterization of relevant terms (covalent and electrostatic)	Electronic structure properties (excited states, transition structure) cannot be accurately modeled due to lack of electron-dependent data	Enzymatic activity, bond formation/breaking, structural changes upon optical excitation with quantum mechanical integration	Ligand docking simulations, design strategies for computational drug design	Docking/interaction studies of self-assembling macromolecules, synthetic proteins
New force fields or modifications to existing force fields can be generated rapidly using experimental or theoretical methods	False minima prediction and the absence of structural/chemical knowledge bases can result in the generation of physically unrealistic minimum energy forms	The continued generalization of force fields to many types of chemical systems, periodic solids, etc.	Coarse grain, reduced model simulations that classically parameterize non-atomistic representations of atomic systems	Steric, electrostatic design basis for pseudo-real-time modeling and design of macromolecules, surfaces
Subsection: Reactive Potentials (REBO, AIREBO, BEBOP)				
Capable of modeling bond breaking, bond formation	No differentiation between spin multiplicities; no inclusion of electron-electron repulsion	Parameterization across a larger range of the Periodic Table, modes of atom binding	Surface interactions and atomic deposition, mechanosynthetic simulations	Extension to larger systems, solvent-solute or surface simulations of chemistry
Uses experimental parameters (such as ionization energies) as parameters	Extremely limited range of parameterized atoms, least element-complete MD-based method	Extension to larger unstable/metastable structures beyond quantum chemical feasibility	MD-based simulations of chemical (solution-phase) phenomena (bond breaking, formation)	Simulations of atomistic nanoscale mechanical processes, including tribological studies

Table-1.3.Modeling, Design, and Characterization of Nanosystems Using Empirical Methods

Capabilities	Limitations	Projected Advances	Typical Applications	Projected Applications
Subsection: General Types – >1000 Atoms				
Semi-empirical methods are fast and far more computationally reasonable than ab initio calculations				
Subsection: CNDO, INDO, MNDO, MINDO/3, ZINDO, AMI, PM3, MNDO/d, OM1,OM2, PM5, RM1				
Computational cost of integral evaluation in *ab initio* methods is replaced by parameter-based evaluation, saving considerable computation time	The many limitations and known failures of semi-empirical methods are inherent to the approach. Their utility in chemical design is dependent on the properties being considered.	Application in solid-state chemistry for the property prediction of molecular and atomic solids (phonons and thermochemistry, nonlinear optical properties)	Most every commercial molecular modeling package includes semi-empirical methods because of their speed and molecular accuracy, making them broadly applied	Stepping-stone computational approaches to higher-level calculations, dry-run methodological studies in combined QM/MM studies
Non-nearest-neighbor interactions are neglected, yielding significant speed-ups in calculations of large systems (with many electrons)	As a parameterized approach based on sets of common molecules, molecules that deviate significantly from these sets (non-common organics, non-biological molecules, etc.) are subject to greater errors	Linear-scaling implementations (MOZYME) for initial quantum chemical optimizations and property prediction of macromolecules (proteins and beyond)	Rapid prototyping of molecules, transition states, excited state geometries, functional groups, and some classes of aggregate and intermolecular interactions	In the absence of MM/MD methods that have parameters for constituent atoms, semi-empirical methods become the route to energy minimization and structural studies
Lowest level of quantum chemical theory to provide chemically relevant information for molecules	Molecular properties that were not addressed in the parameterization process are not (or are poorly) accounted for (such as excited states)	Implementation of methods that consider transition metals for organometallic studies, inorganic solid studies	Prediction of electronic spectra (ZINDO), molecular vibrations, heats of formation, conformational energies	Application to quantum chemical studies of entire proteins and DNA structures (already possible)
More recent semi-empirical methods account for intermolecular interaction energies and geometries	Each semi-empirical level of theory is limited to regions of the Periodic Table (with transition metals neglected in many parameterization sets)	Implementation as the quantum mechanical component of QM/MM studies for rapid prototyping of nanoscale processes	Structure prediction and optimization (geometry beautification) prior to more computationally-demanding *ab initio* studies	Tool for solid-state crystal predictions, study of polymorphism in molecular solids, assembly processes at surfaces

Table-1.4.Modeling, Design, and Characterization of Nanosystems Using Semi-Empirical Methods

Capabilities	Limitations	Projected Advances	Typical Applications	Projected Applications
Subsection: Hartree-Fock (RHF), Unrestricted HF (UHF), R-Open-Shell HF (ROHF), >100 Atoms				
Chemically logical interpretation of electronic structure calculations is possible via orbital-based methods	The lack of static electron correlation (beyond the Pauli exclusion principle) results in inaccurate predictions of spin states and energies	The use of HF theory as a tool for computational chemistry is dependent on algorithms and computational resources at large scales	Reasonable level of theory for survey-type computational studies of molecules and strongly interacting molecular clusters	First, most likely level of theory for first-principles quantum chemical calculations of nanoscale structures
Isodesmic energy calculations of chemical systems (direct comparisons of conformations, reactants, and products with identical basis sets)	The lack of dynamic electron correlation means dispersion energies are predicted to be too low, affecting the calculated strengths of intermolecular interactions	The key improvement to HF application in nanoscience is extension of the calculations with larger basis sets (Slater-type orbitals, all-electron sets for metals, effective core potentials for transition metals, etc.)	As no parameters are used and classes of basis sets do exist that account for most every element in the periodic table, property prediction is possible for nearly all molecules	Stepping-stone computational approaches to higher-level calculations, dry-run methodological studies in combined QM/MM studies
Reasonable scaling (N^3 possible. As implemented in many programs, N^4 scaling; N = number of basis functions) compared to post-HF methods.	When electronic states are close in energy at certain atomic geometries, the Born-Oppenheimer approximation breaks down, requiring the use of " non-adiabatic" (nuclear/electronic) wavefunctions	As the foundation for post-HF methods, any developments in non-DFT electron correlation methods will involve developments in HF (scaling of systems, parallelization of calculations)	The HF solution (wavefunction) is the formal basis for numerous electron correlation methods, variational methods	In the absence of MM/MD methods that have parameters for constituent atoms, HF methods become the route to energy minimization and structural studies
Most fundamental and theoretically sound quantum chemical treatment of molecules	Unoccupied orbital energies are not predicted well due to absence of electron correlation, making excited state and transition state calculations suspect	As the basis for hybrid HF-DFT methods ("B3LYP"), extension of these DFT approaches will follow from general improvements in HF algorithms	Rapid generation of molecular orbital descriptions for interpretive, predictive studies of chemical systems, organic chemistry reactions	In the absence of semi-empirical methods that have parameters for constituent atoms, HF methods become the fastest route to energy minimization and structural studies
The foundation for all post-HF quantum chemical methods	Chemical bond breaking and molecular dissociation are not accurately modeled	Advances in scaling and parallelization will enable HF application in macromolecule studies and, eventually, nanoscale studies	Common quantum chemical method for use in QM/MM studies of enzymatic activity, chemical assembly processes	Nanoscale simulations that do not involve changes in electron spin as part of structural changes

Table-1.5.Modeling, Design, and Characterization of Nanosystems using ab initio (Hartree-Fock) Methods

Capabilities	Limitations	Projected Advances	Typical Applications	Projected Applications
Subsection: LAD (PWC, VWN)—>100 Atoms				
LDA - local density approximation, uses the density at points for evaluation of matrix elements				
Subsection: GGA (such as LYP, P86, B88, BP, BLYP, BOP, HCTH) —>100 Atoms				
GGA - generalized gradient approximation - uses both position and gradient of density at that position (corrects LDA over-binding)				
Subsection: Hybrid HF-DFT (such as B3LYP, B3P86) —>100 Atoms				
DFT electron correlation based on HF wavefunctions				
Static electron correlation is included in DFT calculations, recovering more of the real energy of molecules than HF methods	Static-only electron correlation means dispersion forces are not accounted for correctly, leading to the under-prediction of binding energies for weak complexes	The most important DFT limitation is the absence of dispersion forces. Numerous modeling efforts are directed at including these forces into calculations	Virtually all molecular properties are obtainable by DFT calculations, with accuracy limited by the absence of dispersion and the lack of classes of excited state density functionals	Better property prediction than HF methods for nanoscale simulations, far faster than post-HF methods for studies in the same size regime
Implementations for atom-centered (atomic basis sets) and planewave (periodic boundary condition) codes	Density functionals are derived empirically. Therefore, dozens of density functionals exist that all have strengths and weaknesses.	Dispersion force inclusion by way of the addition of empirical dispersion terms, inclusion within pseudopotentials, hybrid DFT/MPn methods	Solid-state property prediction, including geometries, phonon calculations, binding energies, general thermodynamics properties	Continued extension to the study of solid-state materials, including molecular crystals and amorphous solids
The most cost-effective (resource-based) electron correlation method available for a given level of accuracy	The molecular property in question determines the best choice of density functional at a given level of theory and choice of basis set	Linear scaling approaches to reduce the computational cost of macromolecular system and nanostructure studies	Implementations of time-dependent DFT for property prediction (electron transport through molecules, excited states, electron/molecule scattering)	Greater accuracy of deposition processes than HF methods, meaning the complete and accurate modeling of mechanosynthetic systems is possible
As commonly implemented, N^4 scaling achievable (N = number of basis functions)	Density functionals are developed for ground state systems. Excited-state DFT calculations are fundamentally suspect because of this.	Development of new density functionals for excited electronic state studies of molecules and nanostructures	Car-Parrinello molecular dynamics implmentations already allow for DFT-MD studies of solids, aggregates, conformational space sampling	With fully implemented time-dependent DFT, photophysical studies, dynamical studies, molecular electronics design and simulation becomes possible

Table-1.6.Modeling, Design, and Characterization of Nanosystems Using Density Functional Theory

Capabilities and Limitations, Method Summary	Scaling
Subsection: Moeller-Plesset Perturbation Theory (MP*n*)	
Inclusion of dynamic electron correlation means dispersion forces are accounted for in the optimization of weak intermolecular complexes and some intramolecular interactions	$n = 2$, M^5 $n = 3$, M^6
80% to 95% of the electron correlation of a system is recoverable depending on the order of the calculation (80% at n = 2; 95% at n = 4)	$n = 4$, M^7
Non-variational method, leading to greater basis set superposition error (BSSE) and reduced accuracy of intermolecular interaction energies, over-binding of some systems, over-stabilization of free radicals	
Subsection: Configuration Interaction (CI)	
Static and dynamic electron correlation method based on the expansion of a reference wavefunction into excited-state electronic configurations	
Complete CI calculations can achieve the exact solution to the non-relativistic Born-Oppenheimer approximation Schrodinger equation at considerable computational cost.	
Various levels of CI can be implemented in a calculation, including: CI with single electron configurations (CIS, excellent basis for electronic spectra prediction) CI with single and double electron configurations (CISD) Quadratic CI, all single and double configurations and perturbative inclusion of triple excitations (QCISD(T)) Multi-Reference CI (MRCI) CI with single, double, triplet, quartet configurations (CISDQT)	 M^5 M^6 M^7 M^8 M^{10}
Subsection: CBS/Extrapolation Methods	
Complete basis set/extrapolation methods are excellent for the accurate calculation of reaction barriers, depositions	M^7
Subsection: G2, G3	
Used to calculate thermodynamic quantities such as enthalpies of formation, atomization energies, ionization energies, and electron affinities	M^7
Subsection: Multi-Configuration Self-Consistent Field (MCSCF)	
Full CI and orbital optimizations, used for bond breaking, forming, ground-excited state calculations,	M^7
Recovers much of the static correlation energy (dynamic correlation energy obtained from CI)	
The choice of the active space to include in the calculation is not always obvious (not a black box approach, you still have to know some quantum theory)	
Subsection: Complete Active Space Self-Consistent Field (CASSCF)	
Excellent reference calculations for recovering dynamical correlation energy	M^7
The "active space" of the calculation is defined by the user, requiring testing or considerable understanding of the system and method	
Subsection: Coupled Cluster (CC)	
Possible to achieve the exact solution to the Schrodinger equation for a given basis set at high enough levels	
CC including double excitations only (CCD) CC including single and double excitations (CCSD) CC including single and double excitations with triple excitations treated approximately (CCSD(T)) CC including single, double, and triple excitations (CCSDT)	M^5 M^6 M^7 M^8
Subsection: Generalized Valence Bond (GVB)	
A limited form of MCSCF, multi-reference method	
GVB-Perfect Pairs (GVB-PP) GVB-Restricted Configuration Interaction (GVB-RCI)	
Subsection: Quantum Monte Carlo (QMC)	
Evaluation of integrals with correlated basis functions numerically using Monte Carlo methods	Indet.
Scaling values are approximate, highly method-dependent, and provided as the information is available. Provided values are only for estimation purposes; M = number of electrons	

Table-1.7.Modeling, Design, and Characterization of Nanosystems Using Post Hartree-Fock Methods

2.9. Instrumentation and Characterization

Instrumentation and characterization techniques are being driven forward by scientific research requirements, and their applications in developing AP nanosystems chiefly add to this existing demand. This section offers a few remarks regarding the relationship between this area and the requirements for AP nanosystem development. The takeaway message is that existing techniques are broadly adequate, but that improvements in some areas could be of great value. Characterization of structure and functional properties is critical to developing components and systems on any scale, including the nanoscale. Individual high-spatial-resolution methods typically provide a subset of the total structural information desired, and artifacts and ambiguities are a pervasive vulnerability, commonly addressed by applying multiple methods to a single problem. Improvements in breadth, robustness, and precision of characterization tools are important because they can speed acquisition and improve the quality of information about products. This, in turn, can improve models and enable faster cycles of design and testing in the development process. For example, characterization is often the bottleneck in design cycles for both DNA and protein engineering. Some of these challenges could be addressed by improvements in the capabilities and the availability of cryoelectron tomography instruments.

2.9.1. Atomic-Scale Characterization

Methods that provide lower-resolution information about the nature and distribution of properties in a collection of nanoscale objects sometimes provide the necessary answers for a design process. For example, in structural DNA nanotechnology, overall geometry at or near the helix level often suffices to indicate success or failure in making a structure, and most of the atomic-scale detail is then implied by general knowledge of DNA structures. Nontheless, atomic-scale characterization is of obvious importance to atomic-scale technologies, and a wide range of methods exist. **Table-1.8** provides an overview of techniques and instruments.

2.9.2. Quality Control

There is a need to develop deployable process-monitoring tools that can be used to ensure nanomaterial and nanoproduct consistency on a manufacturing scale. Such instruments would include real time, on-line characterization tools and rapid quality control (QC) tests for samples. Real-time, in-line measurement techniques are needed to provide reproducible control of properties such as particle size and distribution. Improved analytical tools and process control will go a long way to achieving zero defects in final materials, reducing waste, and turning nanomaterial manufacturing into a commodity.

2.9.3. Access to Tools and Multidisciplinary Effort

The need to apply multiple analysis methods stretches the ability of many researchers and students and should encourage collaboration and the use of centralized user facilities. Examples in the US include the DOE Nanotechnology User Facilities and the DOE Environmental Molecular Sciences Laboratory. The R&D effort as a whole must closely interweave developments in fundamental understanding of nanoscale properties, new materials synthesis methodologies, new manufacturing techniques, new characterization and control techniques, and new modelling tools. Progress in nanosystems development requires iterative cycles of design, modelling, fabrication, and characterization. All these steps are

Necessary and each step and field of application presents a rich and diverse set of multi-disciplinary challenges.

Method	Sample Requirements	Information Gained	Comments and Caveats
Scanning Electron Microscopy (SEM)	Placement/deposition on substrate; high vacuum compatible method	Particle size, morphology, component segregation	Must be conductive or coated (e.g., with Gold); Sample must be stable in the electron beam
Environmental SEM	Placement/deposition on substrate; high vacuum compatible method	Particle size, composition, hygroscopicity	Lower resolution in wet mode; Same general issues as SEM
Focused Ion Beam SEM	Typically up to 1" thick, up to 8" diameter	Topography, 3-D composition, crystallography	Excellent for TEM sample preparation as well
Transmission Electron Microscopy/High Resolution TEM	Placement/deposition on substrate; high vacuum compatible method < ~150 nm thick	Phase and structure, composition, chemical state in some cases	Excellent spatial resolution; Sample must be stable in the electron beam
Cryo-Electron Tomography	< ~100 nm thick	3-D structure (tomography)	Can be chemically specific (for example, a gold nanoparticle label)
X-ray Diffraction, Powder X-Ray Diffraction	On substrate (film ~20nm), as a powder (~0.1g), or as single crystals	Crystalline phase, average crystallite size, amorphous content, crystal lattice constants (space group), molecular geometry	-193 to +1000 °C temperature range; Inert atmosphere or rough vacuum sample environment
3-D Atom Probe	Conductive, needle shaped UHV compatible	3-D reconstruction of sample including minor elements to 0.1 atom %	Very high resolution; Sample preparation is often challenging
Scanning Helium Ion Microscopy	Vacuum compatible method	Topography, chemical contrast	Early stage commercialization
Secondary Ion Mass Spectrometer (NanoSIMS)	Flat, <9mm thick UHV compatible	Atomic/isotopic distribution	Usually coat sample with gold; ~50 nm resolution
Scanning Probe Microscopy[1]	Placement/deposition on substrate; Requires a fairly flat sample	Topography, nanoparticle size, shape, electrostatic, magnetic and mechanical properties	Excellent spatial resolution; low sample numbers; slow scan speeds; air, liquid or vacuum environment
Auger Electron Spectroscopy/Scanning Auger Microscopy	Placement/deposition on substrate; high vacuum compatible method	Size, shape, surface composition, 3-D composition	Conductive sample ~20 nm resolution
X-ray Photoelectron Spectroscopy	Placement/deposition on substrate; high vacuum compatible method	Average surface composition, chemical state	Modeling of complex systems improves understanding
Time of Flight Secondary Ion Mass Spectrometry	Placement/deposition on substrate; high vacuum compatible method	Average surface composition, molecular state	Molecular information; good at measuring trace contaminants ~100 nm resolution
Small Angle X-ray and Neutron Scattering	Particles in liquid	Local chemical environment, geometry and size of nanoparticles, clustering of nanoparticles	Requires synchrotron sources
X-ray Absorption Fine Structure	Particles in liquid	Oxidation state, solvation structure	Requires synchrotron sources
Proton Induced X-ray Emission	Placement/deposition on substrate; high vacuum compatible method	Elemental composition	Sample must be stable in the particle beam

Table-1.8.Characterization Methods, Sample Requirements, and Information Obtained

Table-1.8.Continued.....

Method	Sample Requirements	Information Gained	Comments and Caveats
Terahertz (THz) Spectroscopy	Solid-state, in liquid, ambient conditions	Low-frequency vibrational modes, inter- and intramolecular interactions	Many solvents are good THz absorbers (limits utility); resolution currently limits use
Raman Spectroscopy	Airborne, in solution, as solid-state samples, or deposited/mounted on substrate	Energies of vibrational modes, molecular conformation, inter- and intramolecular interactions	Low signal/noise; optical selection rules make for partial determination of molecular vibrations
Fluorescence Resonant Energy Transfer	Ambient, in liquid	Intermolecular distance	Fluorescent tag required
Fluorescence Return After Photobleaching	Ambient, in liquid	Diffusion, clustering using fluorescent probes or auto-fluorescent species	Used in biological systems
Fourier Transform Infrared Spectroscopy	Airborne, in solution, as solid-state samples, or deposited/mounted on substrate	Energies of vibrational modes, molecular conformation, inter- and intramolecular interactions	Low signal/noise; optical selection rules make for partial determination of molecular vibrations
Ultraviolet-Visible Spectroscopy	Airborne, in solution, as solid-state samples, or deposited/mounted on substrate	Electron transition states, survey of potential photochemistry, optical properties	Important characterization tool for molecular electronics applications
Coherent and incoherent inelastic neutron scattering spectroscopy (CINS, IINS)	Solid-state and powder samples	Normal modes of vibration, phonon (intermolecular) modes, molecular geometry via selective deuteration (IINS)	Absence of optical selection rules means all vibrations are observed; resolution limits at higher energies (>1000 cm^{-1})
Nuclear Magnetic Resonance (NMR)	Molecules, macromolecules in solution; selective for many isotopes (such as ^{1}H, ^{10}B, ^{11}B, ^{13}C, ^{14}N, ^{15}N, ^{17}O, ^{19}F, ^{23}Na, ^{29}Si, ^{31}P, ^{35}Cl, ^{195}Pt)	Inter- and intra-molecular structure, atomic connectivity, geometry of secondary structure, monitoring progress of chemical reactions	Experiments can take hours to days for high quality spectra; Two-dimensional methods available (COSY, EXSY, HSQC, HMQC, HMBC, NOESY, TOCSY, J-spectroscopy)
Solid State NMR	Solid-state samples; selective for many isotopes	Molecular structure, local chemical and magnetic environment	Disordered solids, interfaces can be analyzed; *operando* monitoring is a possibility
Dynamic Laser Light Scattering[2]	Particles in liquid	Size distribution down to 5 nm	Light must not be absorbed by liquid; Typically very low ionic strength liquid
Phase Analysis Light Scattering	Particles in liquid	Charge state of particle	Large ionic strength dynamic range
Disc Centrifuge Photosedimentation	Particles in liquid	Size distribution down to 3 nm	Broad range of particle size determination in complex mixtures

3. Microelectromechanical System

3.1. Introduction to Microelectromechanical System

Microelectromechanical systems (MEMS) (also written as micro-electro-mechanical, MicroElectroMechanical or microelectronic and microelectromechanical systems) is the technology of very small devices; it merges at the nano-scale into nanoelectromechanical systems (NEMS) and nanotechnology. MEMS are also referred to as micro machines (in Japan), or micro systems technology – MST (in Europe). MEMS are separate and distinct from the hypothetical vision of molecular nanotechnology or molecular electronics. MEMS are made up of components between 1 to 100 micrometres in size (i.e. 0.001 to 0.1 mm), and MEMS devices generally range in size from 20 micrometres (20 millionths of a metre) to a millimetre (i.e. 0.02 to 1.0 mm). They usually consist of a central unit that processes data (the microprocessor) and several components that interact with the outside such as micro sensors. [52] At these size scales, the standard constructs of classical physics are not always useful. Because of the large surface area to volume ratio of MEMS, surface effects such as electrostatics and wetting dominate volume effects such as inertia or thermal mass. The potential of very small machines was appreciated before the technology existed that could make them—see, for example, Richard Feynman's famous 1959 lecture There's Plenty of Room at the Bottom. MEMS became practical once they could be fabricated using modified semiconductor device fabrication technologies, normally used to make electronics. These include moulding and plating, wet etching (KOH, TMAH) and dry etching (RIE and DRIE), electro discharge machining (EDM), and other technologies capable of manufacturing small devices. An early example of a MEMS device is the resonistor – and electromechanical monolithic resonator [53, 54]

3.2. Materials for MEMS manufacturing

The fabrication of MEMS evolved from the process technology in semiconductor device fabrication, i.e. the basic techniques are deposition of material layers, patterning by photolithography and etching to produce the required shapes.[55]

Silicon

Silicon is the material used to create most integrated circuits used in consumer electronics in the modern world. The economies of scale, ready availability of cheap high-quality materials and ability to incorporate electronic functionality make silicon attractive for a wide variety of MEMS applications. Silicon also has significant advantages engendered through its material properties. In single crystal form, silicon is an almost perfect Hookean material, meaning that when it is flexed there is virtually no hysteresis and hence almost no energy dissipation. As well as making for highly repeatable motion, this also makes silicon very reliable as it suffers very little fatigue and can have service lifetimes in the range of billions to trillions of cycles without breaking.

Polymers

Even though the electronics industry provides an economy of scale for the silicon industry, crystalline silicon is still a complex and relatively expensive material to produce. Polymers

on the other hand can be produced in huge volumes, with a great variety of material characteristics. MEMS devices can be made from polymers by processes such as injection moulding, embossing or stereo lithography and are especially well suited to micro fluidic applications such as disposable blood testing cartridges.

Metals

Metals can also be used to create MEMS elements. While metals do not have some of the advantages displayed by silicon in terms of mechanical properties, when used within their limitations, metals can exhibit very high degrees of reliability. Metals can be deposited by electroplating, evaporation, and sputtering processes. Commonly used metals include gold, nickel, aluminium, copper, chromium, titanium, tungsten, platinum, and silver.

Ceramics

The nitrides of silicon, aluminium and titanium as well as silicon carbide and other ceramics are increasingly applied in MEMS fabrication due to advantageous combinations of material properties. AlN crystallizes in the wurtzite structure and thus shows pyroelectric and piezoelectric properties enabling sensors, for instance, with sensitivity to normal and shear forces. **[56]** TiN, on the other hand, exhibits a high electrical conductivity and large elastic modulus allowing realizing electrostatic MEMS actuation schemes with ultrathin membranes. **[57]** Moreover, the high resistance of TiN against bio corrosion qualifies the material for applications in biogenic environments and in biosensors.

3.3. MEMS basic processes

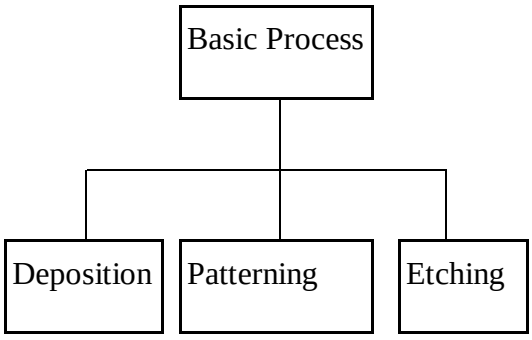


Figure-1.58. Flow diagram of MEMS processes

3.3.1. Deposition processes

One of the basic building blocks in MEMS processing is the ability to deposit thin films of material with a thickness anywhere between a few nanometres to about 100 micrometres.

3.3.1.1. Physical deposition

There are two types of deposition processes. They are as follows.

3.3.1.2. Physical vapour deposition (PVD)

Physical vapour deposition consists of a process in which a material is removed from a target, and deposited on a surface. Techniques to do this include the process of sputtering, in which an ion beam liberates atoms from a target, allowing them to move through the intervening space and deposit on the desired substrate, and Evaporation (deposition), in which a material is evaporated from a target using either heat (thermal evaporation) or an electron beam (e-beam evaporation) in a vacuum system.

3.3.1.3. Chemical deposition

Chemical deposition techniques include chemical vapour deposition ("CVD"), in which a stream of source gas reacts on the substrate to grow the material desired. This can be further divided into categories depending on the details of the technique, for example, LPCVD (Low Pressure chemical vapour deposition) and PECVD (Plasma Enhanced chemical vapour deposition). Oxide films can also be grown by the technique of thermal oxidation, in which the (typically silicon) wafer is exposed to oxygen and/or steam, to grow a thin surface layer of silicon dioxide.

3.3.1.4. Patterning

Patterning in MEMS is the transfer of a pattern into a material.

3.3.2. Lithography

Lithography in MEMS context is typically the transfer of a pattern into a photosensitive material by selective exposure to a radiation source such as light. A photosensitive material is a material that experiences a change in its physical properties when exposed to a radiation source. If a photosensitive material is selectively exposed to radiation (e.g. by masking some of the radiation) the pattern of the radiation on the material is transferred to the material exposed, as the properties of the exposed and unexposed regions differ. This exposed region can then be removed or treated providing a mask for the underlying substrate. Photolithography is typically used with metal or other thin film deposition, wet and dry etching.

3.3.2.1. Electron beam lithography

Electron beam lithography (often abbreviated as e-beam lithography) is the practice of scanning a beam of electrons in a patterned fashion across a surface covered with a film (called the resist), [58] ("exposing" the resist) and of selectively removing either exposed or non-exposed regions of the resist ("developing"). The purpose, as with photolithography, is to create very small structures in the resist that can subsequently be transferred to the substrate material, often by etching. It was developed for manufacturing integrated circuits, and is also used for creating nanotechnology architectures. The primary advantage of electron beam lithography is that it is one of the ways to beat the diffraction limit of light and make features in the nanometre regime. This form of mask less lithography has found wide usage in photo mask-making used in photolithography, low-volume production of semiconductor components, and research & development. The key limitation of electron beam lithography is

throughput, i.e., the very long time it takes to expose an entire silicon wafer or glass substrate. A long exposure time leaves the user vulnerable to beam drift or instability which may occur during the exposure. Also, the turn-around time for reworking or re-design is lengthened unnecessarily if the pattern is not being changed the second time.

3.3.2.2. Ion beam lithography

It is known that focused-ion-beam lithography has the capability of writing extremely fine lines (less than 50 nm line and space has been achieved) without proximity effect. However, because the writing field in ion-beam lithography is quite small, large area patterns must be created by stitching together the small fields.

3.3.2.3. Ion track technology

Ion track technology is a deep cutting tool with a resolution limit around 8 nm applicable to radiation resistant minerals, glasses and polymers. It is capable to generate holes in thin films without any development process. Structural depth can be defined either by ion range or by material thickness. Aspect ratios up to several 10^4 can be reached. The technique can shape and texture materials at a defined inclination angle. Random pattern, single-ion track structures and aimed pattern consisting of individual single tracks can be generated.

3.3.2.4. X-ray lithography

X-ray lithography, is a process used in electronic industry to selectively remove parts of a thin film. It uses X-rays to transfer a geometric pattern from a mask to a light-sensitive chemical photo resist, or simply "resist," on the substrate. A series of chemical treatments then engraves the produced pattern into the material underneath the photo resist.

3.3.3. Etching processes

There are two basic categories of etching processes: wet etching and dry etching. In the former, the material is dissolved when immersed in a chemical solution. In the latter, the material is sputtered or dissolved using reactive ions or a vapour phase etchant. **[59, 60]** for a somewhat dated overview of MEMS etching technologies.

3.3.3.1. Wet etching

Wet chemical etching consists in selective removal of material by dipping a substrate into a solution that dissolves it. The chemical nature of this etching process provides a good selectivity, which means the etching rate of the target material is considerably higher than the mask material if selected carefully.

3.3.3.2. Isotropic etching

Etching progresses at the same speed in all directions. Long and narrow holes in a mask will produce v-shaped grooves in the silicon. The surface of these grooves can be atomically smooth if the etch is carried out correctly, with dimensions and angles being extremely accurate.

3.3.3.3. Anisotropic etching

Some single crystal materials, such as silicon, will have different etching rates depending on the crystallographic orientation of the substrate. This is known as anisotropic etching and one of the most common examples is the etching of silicon in KOH (potassium hydroxide), where Si <111> planes etch approximately 100 times slower than other planes (crystallographic orientations). Therefore, etching a rectangular hole in a (100)-Si wafer results in a pyramid shaped etch pit with 54.7° walls, instead of a hole with curved sidewalls as with isotropic etching.

3.3.3.4. HF etching

Hydrofluoric acid is commonly used as an aqueous etchant for silicon dioxide (SiO_2, also known as BOX for SOI), usually in 49% concentrated form, 5:1, 10:1 or 20:1 BOE (buffered oxide etchant) or BHF (Buffered HF). They were first used in medieval times for glass etching. It was used in IC fabrication for patterning the gate oxide until the process step was replaced by RIE. Hydrofluoric acid is considered one of the more dangerous acids in the clean room. It penetrates the skin upon contact and it diffuses straight to the bone. Therefore the damage is not felt until it is too late.

3.3.3.5. Electrochemical etching

Electrochemical etching (ECE) for do pant-selective removal of silicon is a common method to automate and to selectively control etching. An active p-n diode junction is required, and either type of do pant can be the etch-resistant ("etch-stop") material. Boron is the most common etch-stop does pant. In combination with wet anisotropic etching as described above, ECE has been used successfully for controlling silicon diaphragm thickness in commercial piezoresistive silicon pressure sensors. Selectively doped regions can be created either by implantation, diffusion, or epitaxial deposition of silicon.

3.3.3.6. Xenon difluoride etching

Xenon difluoride (XeF_2) is a dry vapour phase isotropic etch for silicon originally applied for MEMS in 1995 at University of California, Los Angeles.**[61, 62]** Primarily used for releasing metal and dielectric structures by undercutting silicon, XeF_2 has the advantage of a stiction-free release unlike wet etchants. Its etch selectivity to silicon is very high, allowing it to work with photo resist, SiO_2, silicon nitride, and various metals for masking. Its reaction to silicon is "plasma less", is purely chemical and spontaneous and is often operated in pulsed mode. Models of the etching action are available, **[63]** and university laboratories and various commercial tools offer solutions using this approach.

3.3.3.7. Reactive ion etching (RIE)

In reactive ion etching (RIE), the substrate is placed inside a reactor, and several gases are introduced. Plasma is struck in the gas mixture using an RF power source, which breaks the gas molecules into ions. The ions accelerate towards, and react with, the surface of the material being etched, forming another gaseous material. This is known as the chemical part of reactive ion etching. There is also a physical part, which is similar to the sputtering

deposition process. If the ions have high enough energy, they can knock atoms out of the material to be etched without a chemical reaction. It is a very complex task to develop dry etches processes that balance chemical and physical etching, since there are many parameters to adjust. By changing the balance it is possible to influence the anisotropy of the etching, since the chemical part is isotropic and the physical part highly anisotropic the combination can form sidewalls that have shapes from rounded to vertical. RIE can be deep (Deep RIE or deep reactive ion etching (DRIE)).

3.3.3.8. Deep reactive ion etching

Deep RIE (DRIE) is a special subclass of RIE that is growing in popularity. In this process, etch depths of hundreds of micrometres are achieved with almost vertical sidewalls. The primary technology is based on the so-called "Bosch process", **[64]** named after the German company Robert Bosch, which filed the original patent, where two different gas compositions alternate in the reactor. Currently there are two variations of the DRIE. The first variation consists of three distinct steps (the Bosch Process as used in the Plasma-Thermo tool) while the second variation only consists of two steps (ASE used in the STS tool). In the 1st Variation, the etch cycle is as follows: (i) SF_6 isotropic etch; (ii) C_4F_8 passivation; (iii) SF_6 anisoptropic etches for floor cleaning. In the 2nd variation, steps (i) and (iii) are combined. Both variations operate similarly. The C_4F_8 creates a polymer on the surface of the substrate, and the second gas composition (SF_6 and O_2) etches the substrate. The polymer is immediately sputtered away by the physical part of the etching, but only on the horizontal surfaces and not the sidewalls. Since the polymer only dissolves very slowly in the chemical part of the etching, it builds up on the sidewalls and protects them from etching. As a result, etching aspect ratios of 50 to 1 can be achieved. The process can easily be used to etch completely through a silicon substrate, and etch rates are 3–6 times higher than wet etching.

3.3.3.9. Die preparation

After preparing a large number of MEMS devices on a silicon wafer, individual dies have to be separated, which is called die preparation in semiconductor technology. For some applications, the separation is preceded by wafer back grinding in order to reduce the wafer thickness. Wafer dicing may then be performed either by sawing using a cooling liquid or a dry laser process called stealth dicing.

3.4. MEMS manufacturing technologies

3.4.1. Bulk micromachining

Bulk micromachining is the oldest paradigm of silicon based MEMS. The whole thickness of a silicon wafer is used for building the micro-mechanical structures. **[60]** Silicon is machined using various etching processes. Anodic bonding of glass plates or additional silicon wafers is used for adding features in the third dimension and for hermetic encapsulation. Bulk micromachining has been essential in enabling high performance pressure sensors and accelerometers that have changed the shape of the sensor industry in the 80's and 90's.

3.4.1.1. Surface micromachining

Surface micromachining uses layers deposited on the surface of a substrate as the structural materials, rather than using the substrate itself. [65] Surface micromachining was created in the late 1980s to render micromachining of silicon more compatible with planar integrated circuit technology, with the goal of combining MEMS and integrated circuits on the same silicon wafer. The original surface micromachining concept was based on thin polycrystalline silicon layers patterned as movable mechanical structures and released by sacrificial etching of the underlying oxide layer. Interdigital comb electrodes were used to produce in-plane forces and to detect in-plane movement capacitive. This MEMS paradigm has enabled the manufacturing of low cost accelerometers for e.g. automotive air-bag systems and other applications where low performance and/or high g-ranges are sufficient. Analogy Devices have pioneered the industrialization of surface micromachining and have realized the co-integration of MEMS and integrated circuits.

3.4.1.2. High aspect ratio (HAR) silicon micromachining

Both bulk and surface silicon micromachining are used in the industrial production of sensors, ink-jet nozzles, and other devices. But in many cases the distinction between these two has diminished. A new etching technology, deep reactive-ion etching, has made it possible to combine good performance typical of bulk micromachining with comb structures and in-plane operation typical of surface micromachining. While it is common in surface micromachining to have structural layer thickness in the range of 2 µm, in HAR silicon micromachining the thickness can be from 10 to 100 µm. The materials commonly used in HAR silicon micromachining are thick polycrystalline silicon, known as epi-poly, and bonded silicon-on-insulator (SOI) wafers although processes for bulk silicon wafer also have been created (SCREAM). Bonding a second wafer by glass frit bonding, anodic bonding or alloy bonding is used to protect the MEMS structures. Integrated circuits are typically not combined with HAR silicon micromachining. The consensus of the industry at the moment seems to be that the flexibility and reduced process complexity obtained by having the two functions separated far outweighs the small penalty in packaging. A comparison of different high-aspect-ratio microstructure technologies can be found in the HARMST article. A forgotten history regarding surface micromachining revolved around the choice of polysilicon A or B. Fine grained (<300A grain size, US4897360), post strain annealed pure polysilicon was advocated by Prof Henry Guckel (U. Wisconsin); while a larger grain, doped stress controlled polysilicon was advocated by the UC Berkeley group.

3.5. Micro Production Technology

3.5.1. Micro Production System

The Micro Production System developed by Klocke Nanotechnik and partners bridges the gap between nanotechnology and the classical mechanical engineering10. It combines the advantages of both technologies: the backlash free movement with Nanometer resolution and the capability of up to kilograms of load at huge strokes. The included Nanorobotics modules offer plenty degrees of movement and a repeatability of better 50 nm, a value far away from the

The Micro Production System is available in a lot of different levels of complexity. It was the main goal during the development of this system to allow for flexibility:

1. **Modular design**, to be able to add, combine, or exchange components such as force sensors, wafer prober, manipulators, vacuum- and microgrippers or Scanning Probe Microscopes in order to produce different products.
2. **Ability to scale-up the production** beginning from first manually assembled samples up to fully automated mass production.
3. **Process control with an easy to use software**. An example shall detail the second option.

The first step to a product is a prototype that has to be assembled, e.g. with a 4 axis microassembly stage (X, Y, Z-stages plus microgripper) and a joystick. Then about 10-100 prototypes are necessary and some assembly steps should run automatically, e.g. by integrated position sensors and a small software packet. An adhesive dispenser may be added, perhaps also an electrical prober or a Nanofinger.Next step a first production series of 1000-5000 pieces needs more assistance and closed loop operation. Some video cameras and a vision system help to identify micro parts, a base stage and rotary drives arrange these micro parts for the gripper and a sequencer software allows to program complete assembly processes just by “drag and drop”. When prototypes turn into products quality control gets more important and the system can be expanded for example with Scanning Probe Microscopes, nano-indenters, surface inspection systems or wafer probers. The compatible modules of the Nanorobotics series allows this scale-up from a single microgripper over small microassembly stages up to a Micro Production Systems with plenty of different configurations – always with nanoresolution. In the same way the Ethernet-based electronics and modular software can grow with the system.

3.5.1.1. Components of Micro Production System

The Micro Production System includes different groups of positioners, actuators and sensors Shown in

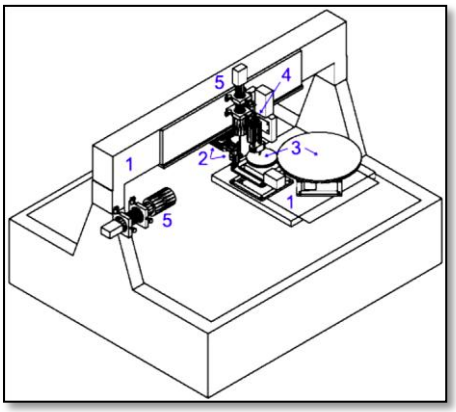


Figure-1.59.Scheme of the Micro Production System:

Point 1:- High precision xy-stage with 100x100 mm2 or 350x350 mm2 stroke from LPKF11, resolution better 200 nm.

Point 2:- Nanorobotics modules, Microgripper, Nanofinger, Waferprober...

Point 3:- Two rotation stages to change the orientation of the source and target area.

Point 4:- Adhesive dispenser, Nanomanipulators, Scanning Probe Microscopes or e.g. a MicroProf® from FRT8.

Point 5:- Video cameras and vision software for pattern recognition with a

resolution of up to 400 nm used for orientation detection and quality control. Up to 6 cameras can be included.

Point 6:- Process control with graphical user interface.

A) Different hardware arrangements

Starting from a microassembly stage made with Nanorobotics modules like shown in

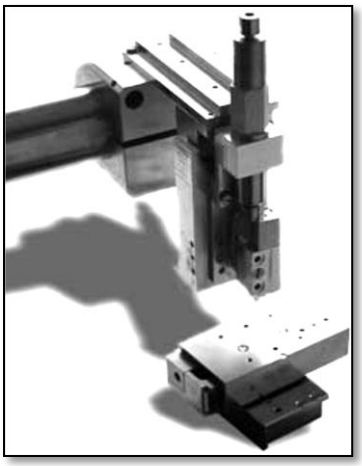


Figure-1.60.Microassembly stage made with Nanorobotics modules, 20 mm stroke each.

over the bottom area is big enough to include a set of Nanorobotics modules that can operate with 5 independent tools. Three video microscope cameras can be fixed at the frame

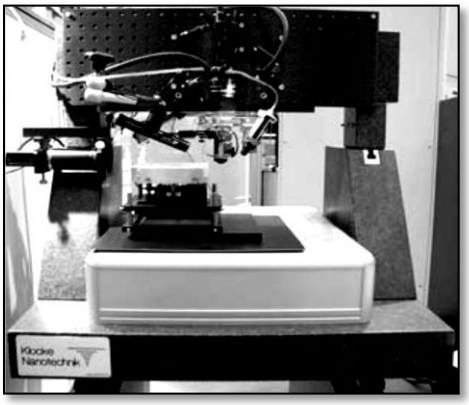


Figure-1.61.When a bigger high precision xy-stage is necessary there are two systems defined by the size of this stage: an xy-stage with 100x100 mm2 stroke

Only one rotary drive fits onto the xy-stage. Source and target area have to fit onto this rotary drive. The bridge components like adhesive dispenser, surface inspection systems or wafer prober can be included. One video camera is fixed on the moving part of the xy-stage for a programmable inspection position

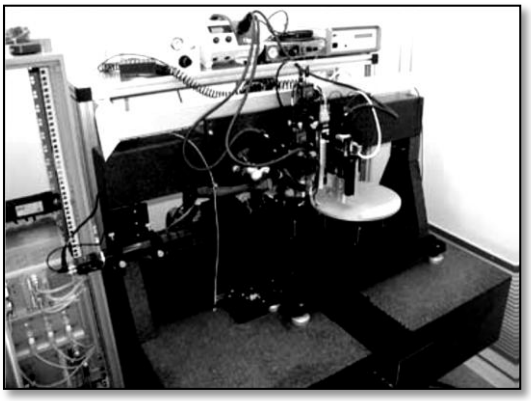


Figure-1.62.Micro Production System with a bigger xy-stage (350x350 mm2 stroke)

Big version with 350x350 mm2 stroke. The bigger xy-stage offers much more space for equipment Two rotary drives can be moved with the bottom xy-stage, one for the source area, the other for the target area. Besides the Nanorobotics modules of the smaller setup many additional This big system can include up to 6 video cameras Both stages have a resolution better 200 nm.

3.5.1.2. Operation Modes and Vision System

The scale-up process is not only made possible by a modular hardware concept. The way from manipulation by hand up to automatic production with vision control is also possible.

The manual mode allows to control all axes of the system with up to 2 (force feedback-) joysticks. Each joystick can move 4 different axes without changing the configuration.

The second level of process control allows to generate sequences over menus and teaching with the manual control program, a programming language is not necessary. In theory microparts are delivered well oriented in carrier structures. But the reality delivers more something like micro chicken food. A flexible assembly system should also be able to handle these objects. Sorting mechanisms to orient these small parts in a flowing process are not always useful, because the microparts stick at these alignment structures by adhesion.

The third level of process control allows to generate a closed loop process including vision control. Up to 6 video microscopes can grab pictures, and a pattern recognition software determines the position of not oriented microparts. Therefore a few millimeter picture size are necessary to keep an overview. At a field of view of 4x3 mm2 the pattern recognition operates with a repeatability of 400 nm.

The Server PC with the vision software includes a command parser that allows a remote control over Ethernet commands from the Client PC. The client PC can switch between different cameras and ask for the position of recognized objects. The transformation from the

coordinate system of the video camera to the world coordinate system is included and invisible for the user.

3.5.1.3. Process Control

The Micro Production System is controlled by a network of computers **(Figure-1.63).** A Client-PC“ is responsible for the global process as a master. A PC with a vision system as well as some embedded server PCs act as slaves and react only on commands from the master. The communication between these parallel operating devices is made by Ethernet.

This structure has two main advantages:

1. Flexible and easily configurable by adding or removing Ethernet-devices.

2. Fast and reliable by parallel operation on different levels.

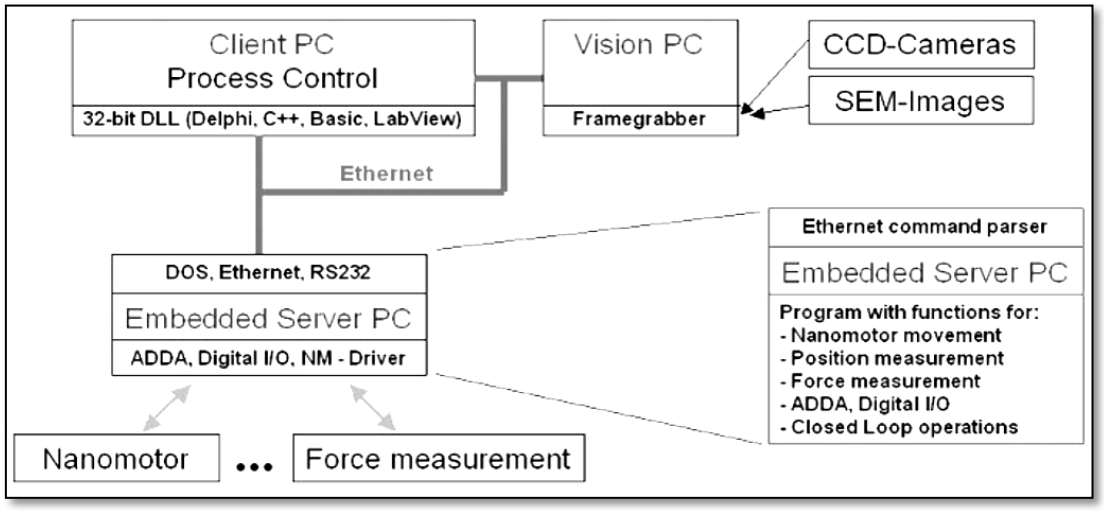


Figure-1.63.Scheme of the Ethernet based process control.

3.5.1.4. Demands for Micro Production Technology

In the last years the demand for ultra-precise production facilities increased rapidly. The revolution in MEMS technology and in communication technology lead to a variety of small objects that have to be assembled and bonded with nano-precision. On the way to new handing and assembly systems a set of tasks has to be fulfilled1:

Task 1: Reproducibility of positioners: better than 1 µm

Task 2: Adjustment of the microparts orientation: better than 20 nm

Task 3: Many degrees of freedom in smallest volume

Task 4: Compatible system of modules

Task 5: Handing over from coarse approach to microassembly

Task 6: Protection of sensitive microparts and grippers (force limitations)

Task 7: Transport “without” gravity

Task 8: Quality control with suitable resolution

Approaches to solve these tasks will be presented in the later section. As an actuator for microtechnology the Nanomotor developed by Klocke Nanotechnik is a central element that allows to solve most of the items listed. It is a linear motor with a positioning stroke of up to some centimeters at atomic resolution. This is a bridge over eight orders of magnitude. The small version of the Nanomotor is half the size of a matchstick and can lift six times its own mass or make indents even into a diamond. The Nanomotor can be combined to many kinds of positioners: From scanning tunnelling microscopes with atomic resolution on a normal table over positioning tables and manipulators up to microassembly stages with different kind of grippers and glue dispensers. It is the driving element for the Nanorobotics series presented below.

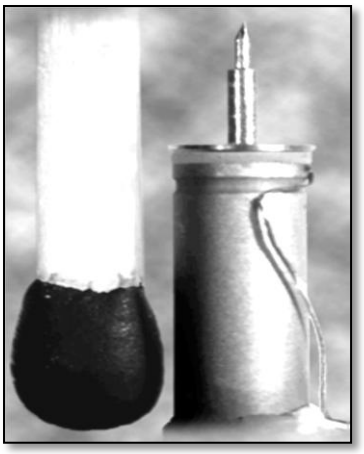


Figure-1.64.The Nanomotor

Task-1 Reproducibility

The assembly line for mobile phone production has a typical movement reproducibility of 20 µm.Special assembly lines are offered with a guaranteed resolution of 10 µm. These systems can be tuned to a reproducibility of about 5 µm by using granite plates at constant temperatures.For glass fiber assembly the demand in reproducibility is 3 µm at the moment, a value that may be achievable. Next generations will need 1 µm and a future-proof system should allow a reproducibility below 1 µm. But thermal expansions in the classical design of meter sized robots and actuators will already avoid a precise positioning. The reproducibility of positioners enclosing Nanomotors is better than 50 nm. The resolution is even much better: atomic without damping systems, see Fig. 2. The picture was taken at a fair with a Scanning Tunneling Microscope (STM) without any vibration damping system. Using a Nanomotor as central element reduces the size and makes the STM insensitive to vibrations.

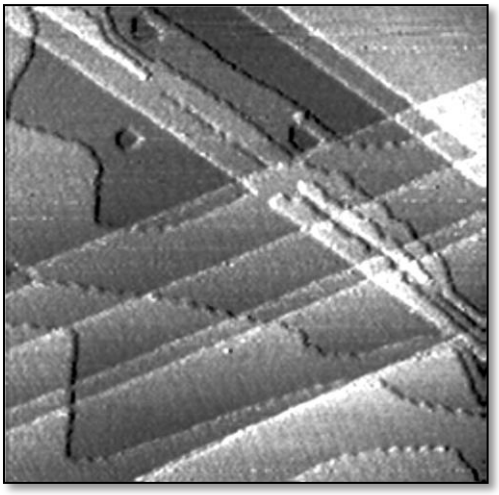


Figure-1.65.Atomic structures of a gold surface

Task-2 Orientation of Microparts

A good reproducibility is only the first step. At the moment when the micropart shall be fixed it is often necessary to adjust its orientation with a resolution far below 1 µm. Sometimes optical fibers have to be aligned with a precision better 10 nm. Sharpen a hair... or bring a tip onto the end of a glass fiber and focus it! This microassembly example of a detection element in Scanning Nearfield Optical Microscopes (SNOM) needs a resolution of better 20 nm2. A Pyramid shaped micro tip is glued onto the end of a glass fiber. A 150 nm small hole in that tip forms a lens as sub-λ light source. The adhesive bonding process requires a very high precision. During the adjustment and the following curing of the adhesive, laser light is coupled through the glass fiber. The light emission of the microtip is measured to control the orientation of the microtip and glass fiber continuously. A misalignment of only 30 nm is clearly visible. The glass fiber with such a pinhole at its end then is assembled beside a shear force sensor. This device is used as central detection element in SNOMs.

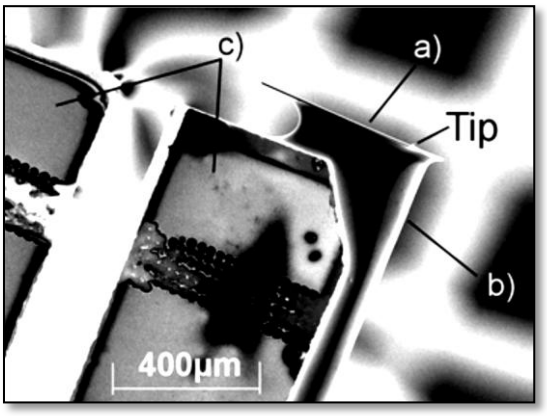


Figure-1.66.Assembled SNOM tip, shows a SEM picture of the assembled parts: a) Cantilever with microtip b) Glass fiber c) Shear force sensor

The amount of adhesive applied between the parts a, b and c is critical: too much adhesive and the shear force sensor is damped. Too little adhesive allows for the cantilever of the

microtip to oscillate freely. In both cases the device would be destroyed. The adhesive is applied with one of the Nanorobotics manipulators,

Task-3 Many degrees of freedom in smallest volume

When the size of a positioning system is doubled, a factor of 16 more acoustic noise will couple into it. A small size is essential to achieve a good resolution without expensive damping systems. For many assembly and handling tasks it is necessary, that a set of different sensors and actuators can move to one point. This point is defined e.g. by the focus of three or more video microscope cameras. The smaller the actuators are the more of them can operate in this area.

Task-4 Compatible system of Modules

For assembly lines, the easy exchange of compatible positioners is necessary to reduce down time. Flexibility is also necessary, when new MEMS products are developed. During development, the assembly stage can vary often in strokes and degrees of freedom. Positioners, microgrippers, adhesive dispensers, or e.g. nano-indenters should be screwed onto each other within some minutes, all controlled with the same network compatible electronics and software. In the last years Klocke Nanotechnik and partners developed a new Nanorobotics system3. Loads of up to two kilogram can be moved over strokes up to 70 mm at resolutions down to 2 nm. This system allows microassembly, interconnection technology, analysis and reliability testing with plenty degrees of freedom in smallest volume without backlash. All Nanorobotics modules can easily be fixed onto each other. Equipped with high resolution position sensors they allow automation with a repeatability far below 50 nm.

The following pictures show examples of the Nanorobotics modules:

Figure-1.67.Linear stage with 10 mm stroke at Resolution of movement:atomic.2 nm resolution, burdened with 2 kg.

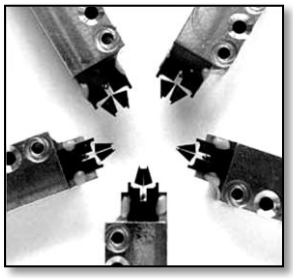


Figure-1.68.A set of micro grippers with different tip

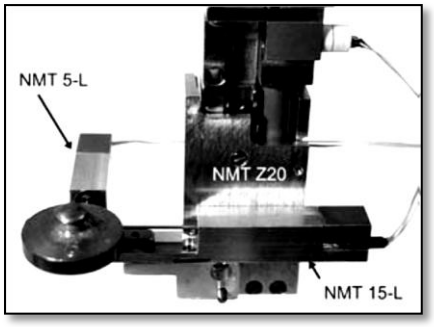


Figure-1.69.A small manipulator with 5 x 15 x 20 mm3 stroke

The combination of a manipulator like shown in Fig 6 and a microgripper (Fig. 5) is already a small microassembly stage.

Task-5 Handing over from Coarse Approach to Microassembly

A glass fiber is a typical object that has to be assembled with (sub-) micron resolution, but comes from a cable drum, perhaps in a machine hall. The robot supplying the glass fiber stops its movement not exactly in the zero position of the microgripper. Pattern recognition systems may help, but they are expensive. The Nanomotor driven microgrippers can solve the problem of handing over from coarse to good accuracy. The gripper structure can grip a fiber even when it is out of the grippers center: Both tips close until one is stopped by the fiber. The second tip continues its movement until the gripper is closed. Then the fiber is released (e.g. by the robot) and the gripper structure moves into its own center position.

Task-6 Protection of Microparts and Grippers

The combination of microassembly stages and microgrippers with classical CNC technology includes miscellaneous risks that may be new for both sides. It is possible to fix a microgripper onto a CNC robot. But what happens, if this robot drives the microgripper a few mm too deep into the table? It happens in practice, for example during setting-up the operation. The microassembly stages made with the Nanorobotics modules are inherently protected against a crash. Each axis posesses a force limitation and the microgripper is designed compatible to this force limit. The gripper can be driven down onto a base plate without damaging its small tips or its bending elements. Horizontal movements slightly hitting the gripper structure against a small wall also do not harm the gripper. The protection of microparts is important as well. A task that required superior sensitivity and manipulation skills was solved at KOSMA4. The assembly of substrate bars for RF devices with a profile of 35 µm x 80 µm could only be done with Nanometer resolution, because coarser tools would have damaged or flipped away the components. The sensitivity of the substrate bars for electrostatic discharge is much higher than the sensitivity of semiconductor devices. The small size of the assembly stage allowed an easy grounding and a secure handling. This assembly stage is now used by RF groups from all over the world to produce high frequency devices (800 GHz or higher).

Task-7 Transport without Gravity

When the size of microparts is smaller than the edge sharpness of a microgripper, other methods of transport should be used. Then, the influence of gravity onto the objects to be handled can be smaller than other forces which in turn can be expolited for the transport. The developments of such processes and tools were made in an electron microscope.

Figure-1.70.The enhancement of the electron microscope from the pure device for analytics to a material processing system was enabled with the Nanomanipulator,

Small as a film cartridge even several manipulators fit into the vacuum chamber. The manipulator can be moved half a cubic centimeter with a resolution of one Nanometer. It can contain various micro tools for cutting, scraping, gripping, spark erosion or for laser ablation. The combination of Nano manipulator and SEM leads to a powerful tool as a workbench. It allows manipulation and even assembly with Nanometer resolution in combination with all kinds of analytical methods (EDX, WDX, EBSP). The sequence of Fig. 8 is an example of handling 1 µm small objects in a SEM. The left manipulator lifts up a cluster of these balls with the first force. The second manipulator captures this cluster with a second higher force. In this case the first force was adhesion, the second magnetism6

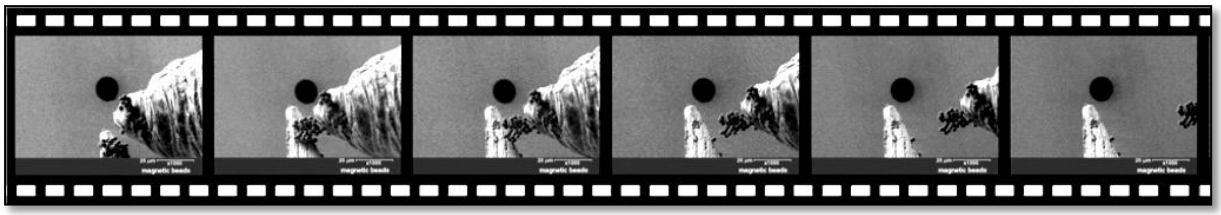


Figure-1.71.Nanomanipulation of magnetic beads

In the handling process of Fig. 9 another force is used7. Electronical drop outs in integrated circuits that result from structural defects can be inspected by high-resolution transmission electron microscopy measurements. This requires to cut a very small lamella out of the drop-out-area.Using Nanomanipulators renders the complicated preparation techniques much easier.

First the Nano manipulator breaks a sample out of a chip structure and then a voltage is applied only to the tip of the Nano manipulator. This additional charge allows to grip the sample and raise it.

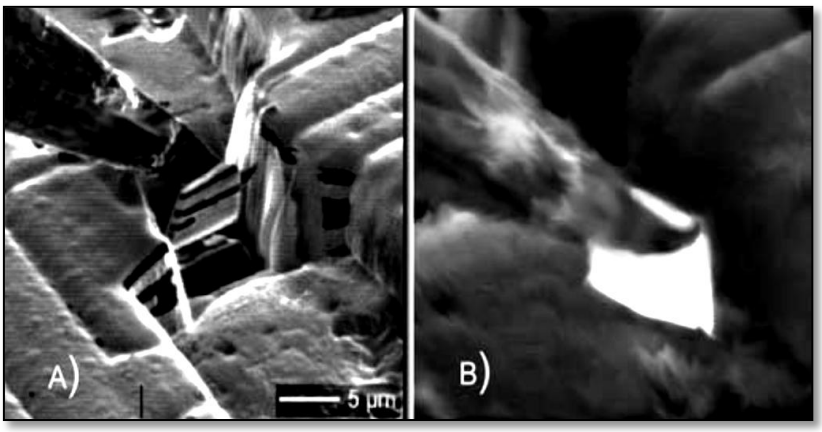


Figure-1.72.Breaking a lamella (A) and lifting it by charge (B).

Task-8 Suitable Quality Control

In classical precision mechanics the device size is about 1 m and the precision is up to 1 µm - a ratio of 6 orders of magnitude. A micropart produced with 0.05 mm size leads to 50 Picometers as comparable precision, one tenth of the radius of a gold atom. Instruments to measure the precision of microparts and the alignment of them should have Nanometer resolution. Some quality control instruments have to face an additional problem: an imprint to measure the hardness of a sample must be much smaller than the micropart that shall be analyzed. But when such a small imprint is made and the micropart is transferred to the analysis instrument that shall measure the depth of that imprint - where is it? If microassembly and quality control can be made in one absolute positioning system many problems are solved at once, see Fig. 11.

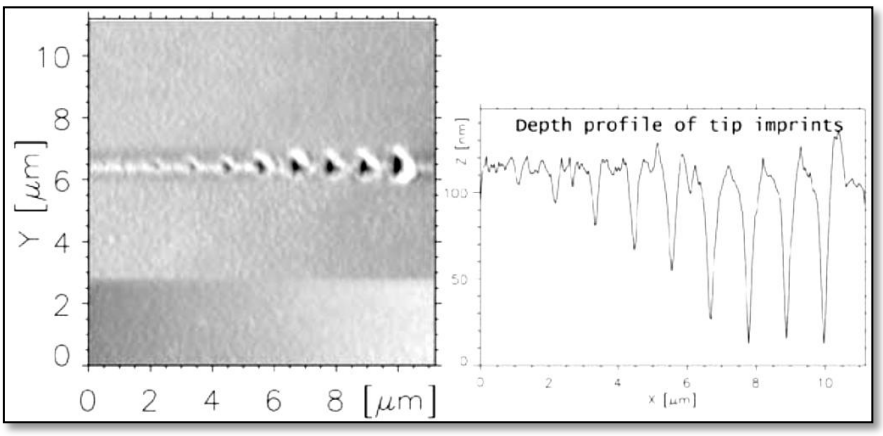


Figure-1.73.Tip imprints made in ruby with a Nanomotor that is the central sensor in an AFM at the same time.Imprint the left image and the depth profile diagram on the right are made with the same device at the same position.

3.5.2. Applications of MEMS

Over the last twenty years, microscale machines have been developed, and their uses are growing rapidly.They currently represent the lowest size limits of commercially available machines. They have small moveable structures such as mirrors, or cantilever beams, which are typically coupled to very small motors that are actuated using electromagnetic induction or electrostatic forces..

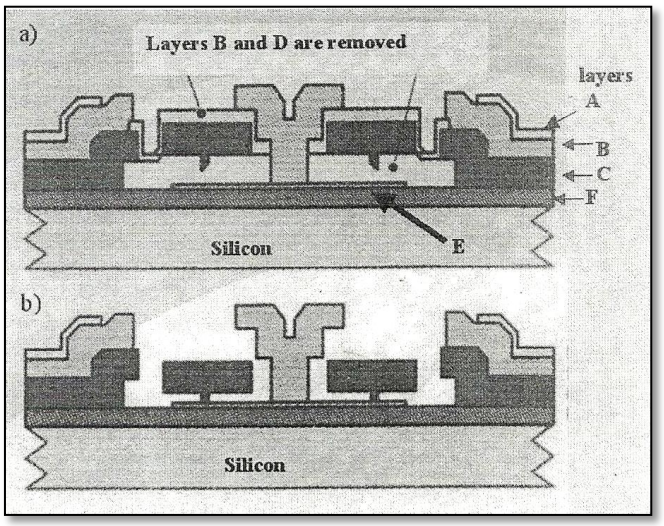


Figure-1.74.shows a cross section of one such device

In this structure, the upper diagram shows layers before etching. The structure is formed by depositing a series of layers (A to D, Figure 9.1a) on top of an insulator (E layer) and silicon substrate, and then etching them away in specific positions so that the structure in Figure 9.1b is formed. The Y-shaped structure in the middle undergoes a seesaw action in which it moves a mirror that allows light to be transferred from one place to another. Layer C is conducting, and hence actuates the Y shape and thus the mirror.

MEMS are largely based on silicon single crystal machining technology, which has evolved from the techniques developed by the microelectronics industry. These are currently used as very sensitive and accurate sensors, small, portable and fast chemical analyzers, and optical switches, but their uses will expand in the future. In time they might also serve as active elements, such as flow controllers in bio-fluid systems.

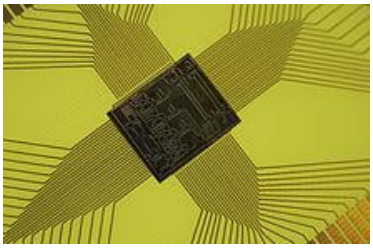


Figure-1.75.Microelectromechanical systems chip, sometimes called "lab on a chip"

In one viewpoint MEMS application is categorized by type of use.

- Sensor
- Actuator
- Structure

In another view point MEMS applications are categorized by the field of application (commercial applications include):

- Inkjet printers, which use piezoelectric or thermal bubble ejection to deposit ink on paper.
- Accelerometers in modern cars for a large number of purposes including airbag deployment in collisions.
- Accelerometers in consumer electronics devices such as game controllers (Nintendo Wii), personal media players / cell phones (Apple phone, various Nokia mobile phone models, various HTC PDA models) **[66]** and a number of Digital Cameras (various Canon Digital IXUS models). Also used in PCs to park the hard disk head when free-fall is detected, to prevent damage and data loss.
- 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 **[67]**
- MEMS microphones in portable devices, e.g., mobile phones, head sets and laptops.
- Silicon 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, which has a surface with several hundred thousand micro mirrors or single micro-scanning-mirrors also called micro scanners
- Optical switching technology, which is used for switching technology and alignment for data communications
- Bio-MEMS applications in medical and health related technologies from Lab-On-Chip to MicroTotalAnalysis (biosensor, chemosensor)
- Interferometric modulator display (IMOD) applications in consumer electronics (primarily displays for mobile devices), used to create interferometric modulation − reflective display technology as found in mirasol displays
- Fluid acceleration such as for micro-cooling

Companies with strong MEMS programs come in many sizes. The larger firms specialize in manufacturing high volume inexpensive components or packaged solutions for end markets such as automobiles, biomedical, and electronics. The successful small firms provide value in innovative solutions and absorb the expense of custom fabrication with high sales margins. In addition, both large and small companies work in R&D to explore MEMS technology.

MEMS have been used as **pressure sensors** since the mid 90s. Until recently, they were primarily used in the management and monitoring of car engines and air conditioning systems. They are also used in accelerometers for a car air bags, ink jet printers, computer hard disk drives ad biomedical analysis. In the near future the use of MEMS as optical cross connect switches and as other opto-mechanics in fiber optic telecommunications networks, will equal and then eclipse the pressure sensor market. Globally, in 2000 MEMS generated US$3.4 billion in sales. This figure will grow to US$31.5 billion in 2010, mainly due to the expected upsurge in telecommunications and other optical work [2]. Cross connect optical switching systems, which will form the hub in the routing system for information and telephone traffic, are Referred to as microoptoelectromechanical system, or MOEMS. This

technology means that light doesn't have to be converted into electrical signal to re-route as it does now. MOEMS technology allows switching light beams with very low loss of light signal power.

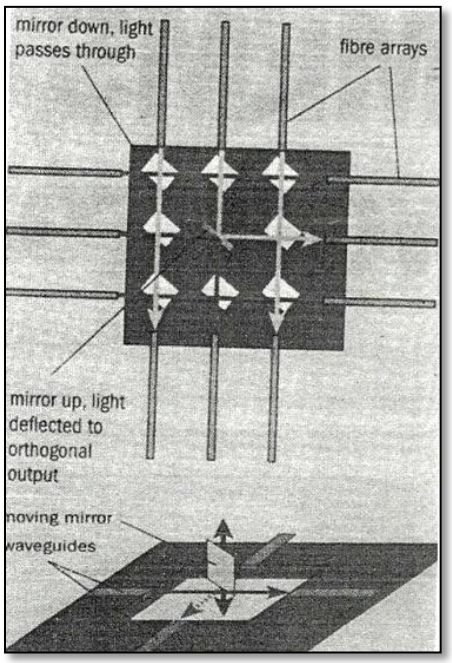


Figure-1.76.shows a MOEM system where a mirror array dictates that a given incoming fibre's light goes almost exactly to the desired output fiber

Array of MOEMS require up to 100 million switchable micro-mirrors at an exchange, although several array will be needed for this, because individual array are unlikely to be this big. However, these machines can be package together and duplicate In large groups, just like transistors on a chip. As an example of what is coming, in 2001 the world's first petabit switch, based on MOEMS, was constructed by Lucent. A petabit is 10^{15} bits per second, or a million gigabits per second. This particular MEM silicon mirror array switches between 1296 ports, each of which carries 40 separate signals, and each of these 40 in carrying data at 40 gigabits per second

Other MEMS-based sensing includes a recently developed highly sensitive magnetic field strength device, where a magnetic field induces distortion and oscillations in very small silicon bar. The distortions are optically monitored. Changes in magnetic field as small as 20 nanotesla can be detected. The earth's magnetic field is about 10^{-4} Tesla, so this MEMS device can detect changes in magnetic field more than a thousand times smaller than the earth's field. Since electrical current produces magnetic fields, currents in our brains or other body areas could be detected with such a device, which by its nature is also very small. Other potential applications of this device include heterodyning (mixing) of oscillating magnetic field signals, electromagnetic filed frequency analysis, and mineral exploration. Chemical and biological sensing can use the effects of different adsorbed species through their different mass, on the vibrational properties of the tiny MEMS plate.

Lab-on-a-chip, or the µChemLab concept uses MEMS and offers a compact way of performing biological and chemical analysis for enviromental, military, medical or home health care with the same sensing ability as large laboratory instruments. This tiny device performs electrochrmatography to separate compounds and/or provide special micro-mirror arrays for separating colours, or different fluoresing nanosize components, which is directed at the smaple. Using this device, ten different explosives and their components have been detected at the 50 ppm level in less than a minute.

Fluid flow control is a major concern in many mechanical systems such as pumps, motors and engines, as well as in much proces equipment, such as heat exchangers and mixing. It is also often useful to be able to vary these flow properties in total or locally. Creating uniform mixing in many proesses can have big benefits. Arrays of MEMS might help by altering and monitoring flow charactersitics in small pipes or blood vessels, in multiple feed networks or in volumes where mixing in weak.

The nanotechnology equivalent of MEMS is nanoelectromechanical systems, or NEMS. These machines already exist in the laboratory, but they are in a very early stage of development. At this stage, work with NEMS has involved using or mimicking naturally occurring biological motors (Chapter 6); nanotubes and related materials; and the molecular mimics . It may be possible to use very small NEMS biomotors to mimic natural movement. Alternatively, artifical mucles could be made using nanoscale bundles of fibres whose individual elastic or conformational properties can be altered at different sections along their length, either chemically or electrically, and possibly also optically, so that bending and gripping ensues. Conducting polymers, such as modifications to polypyrrio and nanotubes may have a role here . Simple movement has already been demonstrated. Althorugh it may be possible for all the functions of MEMS to be taken over by NEMS, some functions can only be performed at the NEMS level.

3.5.3. Industry structure

The global market for micro-electromechanical systems, which includes products such as automobile airbag systems, display systems and inkjet cartridges totaled $40 billion in 2006 according to Global MEMS/Microsystems Markets and Opportunities, a research report from SEMI and Yole Developpement and is forecasted to reach $72 billion by 2011. MEMS devices are defined as die-level components of first-level packaging, and include pressure sensors, accelerometers, gyroscopes, microphones, digital mirror displays, micro fluidic devices, etc. The materials and equipment used to manufacture MEMS devices topped $1 billion worldwide in 2006. Materials demand is driven by substrates, making up over 70 percent of the market, packaging coatings and increasing use of chemical mechanical planarization (CMP). While MEMS manufacturing continues to be dominated by used semiconductor equipment, there is a migration to 200 mm lines and select new tools, including etch and bonding for certain MEMS applications.

4. Nanoelectromechanical System

4.1. Introduction to Nanoelectromechanical System

Nanoelectromechanical systems (NEMS) are devices integrating electrical and mechanical functionality on the nanoscale. NEMS form the logical next miniaturization step from so-called microelectromechanical systems, or MEMS devices. NEMS typically integrate transistor-like nanoelectronics with mechanical actuators, pumps, or motors, and may thereby form physical, biological, and chemical sensors. The name derives from typical device dimensions in the nanometre range, leading to low mass, high mechanical resonance frequencies, potentially large quantum mechanical effects such as zero point motion, and a high surface-to-volume ratio useful for surface-based sensing mechanisms.**[68]** Uses include accelerometers, or detectors of chemical substances in the air.

4.1.1. Overview

Because of the scale on which they can function, NEMS are expected to significantly impact many areas of technology and science and eventually replace MEMS. As noted by Richard Feynman in his famous talk in 1959, there's Plenty of Room at the Bottom, there are a lot of potential applications of machines at smaller and smaller sizes; by building and controlling devices at smaller scales, all technology benefits. Among the expected benefits include greater efficiencies and reduced size, decreased power consumption and lower costs of production in electromechanical systems**. [68].** in 2000, the first very-large-scale integration (VLSI) NEMS device was demonstrated by researchers from IBM. **[69]** Its premise was an array of AFM tips which can heat/sense a deformable substrate in order to function as a memory device. In 2007, the International Technical Roadmap for Semiconductors (ITRS) contains NEMS Memory as a new entry for the Emerging Research Devices section.

4.1.2. Nanomachining

4.1.2.1. Theoretical basis of nanomachining

Scientific study of nanometric machining has been undertaken since the late 1990s. Much attention to the study has been paid especially with the advancement of nanotechnology[52]. The scientific study will result in the formation of the theoretical basis of nanometric machining, which enables the better understanding of nanometric machining physics and the development of its controllable techniques to meet the advanced requirements for nanotechnology and nanoscience.

4.1.2.2. Approaches of Nanomachining

Single-point diamond turning and ultra-precision grinding are They are both capable of producing extremely fine cuts.

4.1.2.2.1. Single-point diamond turning

Single-point diamond turning has been widely used to machine non-ferrous metals such as aluminium and copper. An underformed chip thickness of about 1 nm is observed in diamond turning of electroplated copper.

4.1.2.2.2. Diamond grinding

Diamond grinding is an important process for the machining of brittle materials such as glasses and ceramics to achieve nanometre levels of tolerances and surface finish. A repeatable optical quality surface roughness (surface finish < 10 nm Ra) has been obtained in nano-grinding of hard steel by Stephenson et al. using 76µm grit cBN wheel on the ultra-precision grinding machine tool.

Recently, diamond fly-cutting and diamond milling have been developed for machining non-rotational, non-symmetric geometry, which has enlarged the product spectrum of nanometric machining[47]. In addition the utilization of ultra-fine grain hard metal tools and diamond coated micro tools represents a promising alternative for microcutting of even hardened steel48.

4.1.2.3. Classification of Nanomachinng

Nanomachining can be classified into four categories:

4.1.2.3.1. Deterministic mechanical nanometric machining

The method utilizes fixed and controlled tools, which can specify the profiles of 3D components by a sell-defined tool surface and path. The method can remove materials in amounts as small as tens of nanometers. It includes typically diamond turning micromilling and nano/microgrinding, etc.

4.1.2.3.2. Loose abrasive nanometric machining:

This method uses loose abrasive grits for removal of a small amount of materials. It consists of polishing, lapping and honing, etc.

4.1.2.3.3. Non-mechanical nanometric machining

It comprises focused ion beam machining, micro-Electro Discharge Machining (EDM) and excimer laser machining.

Lithographic method: It employs masks to specify the shape of the product. 2D shapes are the main outcome, severe limitations occur when 3D products are attempted. It mainly includes X-ray lithography, Lithographic Galvano Abformung (LIGA), electron beam lithography.

4.1.2.3.4. Mechanical nanometric machining

It has more advantages than other methods since it is capable of machining complex 3D components in a controllable way. The machining of complex surface geometry is just one of the future trends in nanometric machining, which is driven by the integration of multiple functions in one product. For instance, the method can be used to machine micromoulds and dies with complex geometric features and high dimensional and from accuracy, and even nanometric surface features.

The method is indispensable to manufacturing complex micro and miniature structures, components and products in a variety of engineering materials.

4.1.2.4. Applications of Nanomachining

Early application of nanometric machining are in the mass production of some high precision parts for microproducts, or Microsystems. In fact, microproducts, or microsystems, will be the first path that enables nano-products to enter the marketplace since microproducts, or Microsystems, have been dominating nanotechnology application markets worldwide.

Nanometric machining can be applied in bulk machining of silicon, aluminium substrates for computer memory disks, etc. In other areas such as biomedical, automotive, household and telecommunication the total turnovers of microproducts are still steadily growing.

Nanometric machining is also very promising in the production of sensors, accelerometer, actuators, micro-mirror, fiber optics connectors, and micro-displays. In fact applications of nanoproducts will enhance the performance of microproducts in the form of sensitivity, selectivity and stability. By 2006, IT lost this predominant position owing to new MEMS based applications in sectors such as biotechnology and communication (optical and radio frequency switching, for example, will become a major growth area). Nanometric machining still has priority in this application area. The micro-products are normally integrated products of some electronics, mechanical parts and optical parts while in miniature or micro dimensions. In fact only small number of microproducts solely relies on electronic.

The mechanical and optical parts are of significant importance for microproducts.

4.1.2.5. Advantages of Nanomachining

The indispensable advantage of nanometric machining is its applicability to manufacture 3D complex components/devices including micromoulds, dies and embossing tooling for cheap mass production of optical and mechanical parts. Therefore, it is undoubtedly one to the major enabling technologies for commercialization of nanotechnology in the future.

4.1.3. Nanorobotic System

Two strategies towards the realization of nanotechnology have been presented, i.e., top-down and bottom up. The former one is mainly based on nanofabric tion and includes technologies such as nano-lithography, nano-imprint, and etching. Presently, they are still 2D fabrication

processes with low resolution. The later one is an assembly-based technique. At present, it includes such items as self-assembly, dip-pen lithography, and directed self-assembly. These techniques can generate regular nano patterns in large scales. To fabricate 3D complex nano devices there are still no effective ways by so far. In which, we take a hybrid strategy as shown in **Figure-1.77.**

In this system, nano fabrication and nano assembly can be performed in an arbitrary order to construct nano building blocks and finally nano devices. The most important feature in this system is that the products can be fed back into the system to shrink the system part by part leading to nanorobots. Property characterization can be performed in each intermediate process. Due to the nanorobotic manipulation system, dynamic measurement can be performed rather than conventional static observations.

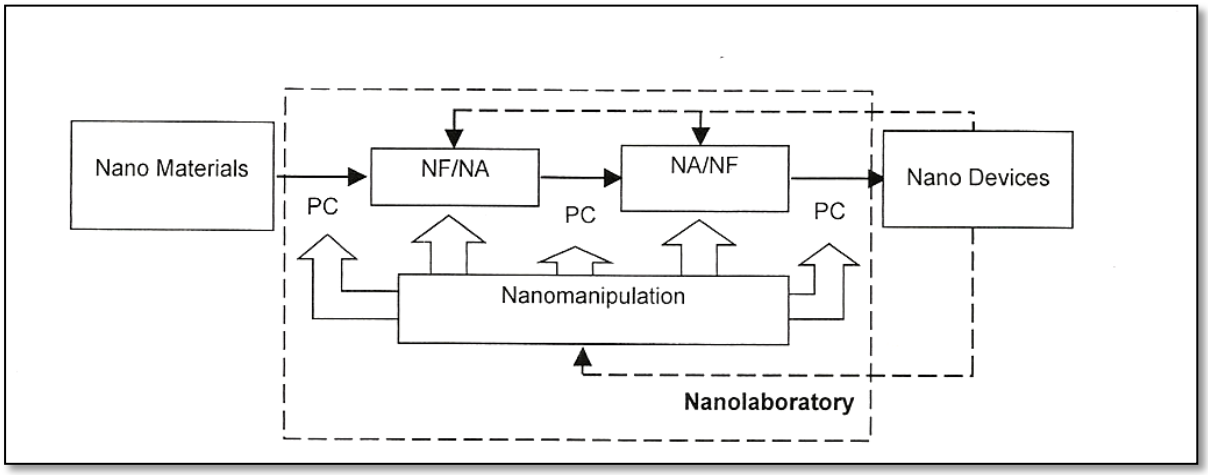


Figure-1.77.Hybrid Strategy for Nano Manufacturing (PC: Property Characterization, NF: Nano Fabrication, NA: Nano Assembly)

4.1.3.1. Materials

4.1.3.1.1. Carbon allotropes

Many of the commonly used materials for NEMS technology have been carbon based, specifically carbon nanotubes and graphene. This is mainly because of the useful properties of carbon based materials which directly meet the needs of NEMS. The mechanical properties of carbon (such as large Young's modulus) are fundamental to the stability of NEMS while the metallic and semiconductor conductivities of carbon based materials allow them to function as transistors. Both graphene and carbon exhibit high Young's modulus, excessively low density, low friction and large surface area.**[71, 72]** The low friction of CNTs, allow practically frictionless bearings and has thus been a huge motivation towards practical applications of CNTs as constitutive elements in NEMS, such as nanomotors, switches, and high-frequency oscillators **[72]** Carbon nanotubes and graphene's physical strength allows carbon based materials to meet higher stress demands, when common materials would normally fail and thus further support their use as a major materials in NEMS technological development. **[73].** Along with the mechanical benefits of carbon based materials, the electrical properties of carbon nanotubes and graphene allow it to be used in many electrical

components of NEMS. Nanotransistors have been developed for both carbon nanotubes **[74]** as well as graphene**. [75]** Transistors are one of the basic building blocks for all electronic devices, so by effectively developing usable transistors, carbon nanotubes and graphene are both very crucial to NEMS.

4.1.3.1.2. Metallic Carbon Nanotubes

Metallic carbon nanotubes have also been proposed for nanoelectronic interconnects since they can carry high current densities. **[73]** This is a very useful property as wires to transfer current are another basic building block of any electrical system. Carbon nanotubes have specifically found so much use in NEMS that methods have already been discovered to connect suspended carbon nanotubes to other nanostructures. **[76]** This allows carbon nanotubes to be structurally set up to make complicated nanoelectric systems. Because carbon based products can be properly controlled and act as interconnects as well as transistors, they serve as a fundamental material in the electrical components of NEMS.

4.1.3.2. Nano Laboratory

In our system, carbon nanotubes (CNTs) have been used as the main materials because of their exceptional properties **(briefly summarized in Table-1.9)** and broad potential applications. In bulk state, nanotubes can be used to synthesize conductive and high-strength composites, to fabricate field emission devices (flat display, lamp, gas discharge tube, x-ray source, microwave generator, etc.), to save and convert electrochemical energy (supercapacitor, battery cathode, electromechanical actuator, etc.), to store hydrogen, and so on. However, the most promising applications of nanotubes that has deepest implications for molecular nanotechnology need to maneuver the tubes individuallyto build complex nanodevices. Such devices include nanoelectronics and nanoelectromechanical systems (NEMS) **(concisely listed in Table-1.10).** Almost all of such applications and many unlisted potential ones of nanotubes for nanoelectronics and NEMS involve charactering, placing, deforming, modifying, and/or connecting nanotubes.Although chemical synthesis may provide a way for patterned structure of nanotubes in large-scale, selfassembly may generate better regular structures, we still lack of capability to construct irregular complex nanotube devices. Nanomanipulation especially nanorobotic manipulation.

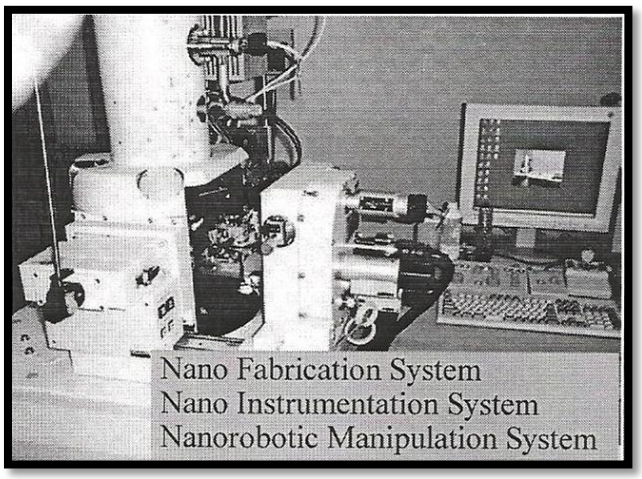


Figure-1.78.Nano laboratory

Property	Item	Data
Geometrical	Layers	Single-walled nanotubes (SWNTs) or Multiwalled nanotubes (MWNTs)
	Aspect Ratio	10-1000
	Diameter	~0.4nm to >3nm (SWNTs) ~1.4 to >100nm (MWNTs)
	Length	Several ìm (Rope up to cm)
Mechanical	Young's Modulus	~1 T Pa (steel: 0.2TPa)
	Tensile Strength	45GPa (steel: 2GPa)
	Density	1.33~1.4g/cm3 (Al: 2.7 g/cm3)
Electronic	Conductivity	Metallic/Semi-conductivity
	Current Carrying Capacity	~1TA/cm3 (Cu: 1GA/cm3)
	Field Emission	Activate Phosphorus at 1~3V
Thermal	Heat Transmission	>3kW/mK (Diamond: 2kW/mK)

Table-1.9.Property of CNT

Device	Fabrication
Diode	Rectifying diode: a kink junction.
Transistor	Room-temperature (RT) field-effect transistors (FETs): a semiconducting SWNT placed between two electrodes (source and drain) with a submerged gate RT single electron transistor (SETs): a short (~20 nm) nanotube section.
ICs	Hybrid logic circuits: two nanotube transistors placed on lithographically fabricated electrodes: Pure nanotube circuits: interconnected nanotubes (intermolecular and intramolecular junctions).
Switch	Pushing and releasing a suspended nanotube
Memory	Electromechanical nonvolatile memory: suspended cross-junctions

Probe	Manually assembly, chemical vapor deposition (CVD), controlled assembly, and picking up a tube from vertically aligned SWNTs.
Tweezers	Assemble two CNT bundles on a glass fiber
Scissors	Nanorobotic assembly and shape modification, Nanorobotic assembly and shape modification

Table-1.10.Applications of CNTs in Nano Devices

which consists of a nanorobotic manipulation system **(Figure-1.78),** an instrumentation system (a filed emission scanning electron microscope (FESEM) and a conventional atomic force microscope cantilever or a piezolever), and a nanofabrication system based on electron-beam-induced deposition (EBID) or manipulations.

Item	Specification
Nanorobotic Manipulation System	
DOFs	Total: 16 DOFs Unit1: 3 DOFs (x, y and β; coarse) Unit2: 1 DOF (z; coarse), 3-DOF (x, y and z; fine) Unit3: 6 DOFs (x, y, z, α, β, γ; ultrafine) Unit 4: 3 DOFs (z, α, β; fine)
Actuators	4 PicomotorsTM (Units 1& 2) 9 PZTs (Units 2& 3) 7 NanomotorsTM (Units 2 & 4)
End-effectors	3 AFM cantilevers+1 substrate or 4 AFM cantilevers
Working space	18mmx18mmx12mmx360° (coarse, fine), 26μmx22μmx35μm (ultrafine)
Positioning resolution	30nm(coarse), 2mrad (coarse), 2nm(fine), sub-nm (ultrafine)
Nano Instrumentation System	
FESEM	Imaging resolution: 1.5 nm
AFM Cantilever	Stiffness constant: 0.03nN/nm
Piezolever	Stain gauge built-in
Nanofabrication System	
EBID	FESEM emitter: T-FE, CNT emitter, Gas introduction system

Table-1.11.The specifications of the nano laboratory .

The nano laboratory can be applied for manipulating nano materials—mainly but not limited to CNTs, fabricating nano building blocks, assembling nano devices, in situ analyzing the properties of such materials, building blocks and devices. The functions of nano laboratory it are summarized in **Table-1.12** and many have been demonstrated elsewhere as shown in the references in the table.

Function	Involved Manipulations
Property Characterization	Mechanical properties: buckling (Dong et al., 2001a) or stretching
	Electric properties: placing between two probes (electrodes)
Nanofabrication	EBID with a CNT emitter and parallel EBID (Dong et al., 2002c)
	Destructive fabrication: breaking (Dong et al., 2001c)
	Shape modification: deforming by bending and buckling, and fixing with EBID (Dong et al., 2001c)
Nanoassembly	Picking up by controlling intermolecular and surface forces, and forces (Dong et al., 2002b)
	Connecting with van der Waals (Dong et al., 2001c)
	Soldering with EBID (Dong et al., 2001c)
	Bonding through mechanochemical systhesis (Dong et al. 2002a)

Table-1.12.Functions of nano laboratory

4.1.3.3. Overview of Nanotube Devices

Interest in creating functional devices at nanometer scales is fueled by the desire to shrink the size of electronic integrated circuits and to create electromechanical systems atnanoscale.CNTs are one of the most important nanomaterials for the fabrication of NEMS including sensors and actuators because of their exceptional properties and special structures.

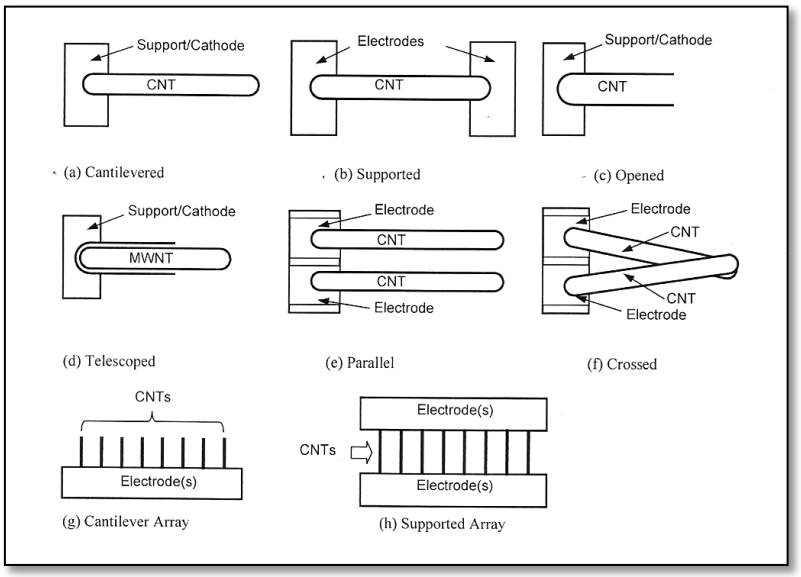


Figure-1.79.Configuration of Nanotube Sensors and Actuators

For detecting deep and narrow features on a surface, cantilevered individual nanotubes **(Figure-1.79.(a))** have been demonstrated as probe tips for an atomic force microscope (AFM), a scanning tunneling microscope (STM) and other kinds of scanning probe microscopes (SPM) because of their ultra small diameters, ultra-large aspect ratios, and excellent elasticity. Cantilevered nanotubes have also been shown as probes for the measurement of ultrasmall physical quantities, such as femto-gram mass , mass flow sensors ,

and pico-Newton order force sensors on the basis of their static deflections or change of resonant frequencies detected with an electron microscope. However, the deflections cannot be measured from micrographs in real-time, which limit the application of this kind of sensors. Inter-electrode distance change caused emission current variation of a nanotube emitter may serve as a candidate to replace the microscope As a typical example, a nanotube proximity sensor .

Cantilevered dual nanotubes (**Figure-1.79 (e) and (f))** are shown as nanotweezers and nanoscissors at first. Based on the electric resistance change under different temperatures, nanotube thermalprobes have been demonstrated for measuring the temperature at an ultra-small site, which is advantageous than the nanotube based thermometer dependent to transmission electron microscope imaging **(Figure-1.79 (c))**

4.1.4. Hybrid Nanorobotic Manipulation System

Nanomanipulation has received much more attention than ever, because it is an effective strategy for the property characterizations of individual nanoscale objects and the construction of nanoscale devices to realize high-integration, multifunction, low-energy consumption, and so on.

To manipulate nanoscale objects, they must be observed with a resolution higher than nanoscale. Hence, a manipulation system and an observation system, e.g., a microscope in general, are necessary for nanomanipulations. Scanning probe microscopes (SPMs), such as scanning tunneling microscopes (STMs) or atomic force microscopes (AFMs), have functions of both observation and manipulation. The feasibility has been shown by the first practice on nanomanipulation demonstrated by Eigler and Schweizer. An STM is applied for positioning individual Xe atoms on a nickel surface with atomic precision at low temperature. Hertel et al. applied an AFM to bend and translate carbon nanotubes (CNTs) on a substrate. Their high resolution makes them capable of atomic manipulation; however, their observation space is too narrow and constrained in a plane.Electron microscopes, such as scanning electron microscopes (SEMs) and transmission electron microscopes (TEMs), show their uniqueness in the capability to contain an independent manipulator inside the specimen chamber for three-dimensional (3-D) manipulation.

High resolution and transmission images of TEMs are useful for the measurement and evaluation of nanoscale objects.Some groups have demonstrated manipulations using a piezotube-driven nanomanipulator inside the specimen holder: Kizuka et al. constructed a manipulator inside a high-resolution TEM (HRTEM) to investigate atomic scale contact and noncontact scanning on gold surfaces. Cumings and Zettl demonstrated a sliding motion between different layers of multiwalled CNTs (MWCNTs) inside a TEM However, the specimen chamber and observation area of the TEM are too narrow to contain manipulators with complex functions. Special sample preparation techniques are also needed. However, the resolution of an SEM is generally one order of magnitude lower than that of a TEM.

Before an ideal microscope can be invented, it is a practical strategy to combine different microscopes so as to take both the resolution and complexities into account A hybrid nanorobotic manipulation system inside a scanning electron microscope (SEM) and a transmission electron microscope (TEM) is presented. The SEM manipulators have been constructed with 8 degrees of freedom (DOFs) with three units for effective TEM sample preparation. The TEMmanipulator consists of a 3-DOF manipulator actuated with four

multilayer piezoelectric actuators and a 3-DOF passively driven sample stage. High resolution and transmission image of TEM is readily used for measurement and evaluation of samples. The stage is pre-manipulated by the SEM manipulator for sample preparations inside the SEM. This methodology is called the hybrid nanorobotic manipulation so as to differentiate it from those with only an exchangeable specimen holder.

To show the effectiveness of the system, the Young's modulus of a carbon nanotube (CNT) was measured to be 1.23 TPa inside a TEM after being premanipulated inside the SEM. With this system, we can measure the inner diameter of a CNT and improve the accuracy in measuring the Young's modulus of a CNT.

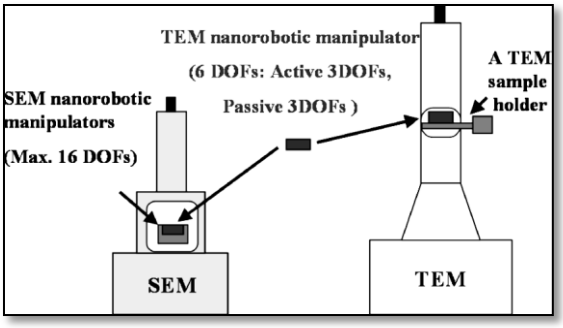


Figure-1.80.Configuration of a hybrid nanorobotic manipulation system

The strategy is called hybrid manipulation so as to differentiate it from those with only an exchangeable specimen holder. The most important feature is that it contains several passive degrees of freedom (DOFs), which makes it possible to perform relatively complex manipulations while a compact volume can be installed inside the narrow vacuum chamber of a TEM

4.1.4.1. Nanomanipulator

As described above, the scanning tunnelling electron microscope has a computer-controlled probe that skates across the surface, and the mechanical deflections are transferred to electrical energy like a vinyl record needle. The probe can also be programmed to push against the surface like a finger. When pushing, the charge separating the flexing tip and its fixed mount creates an electrical current that is proportional to the pressure exerted on the tip. By transmitting this current to the proper computer interface a human can actually do the touching. This instrument is called a nanomanipulator. In its current form it combines a scanning tunnelling electron microscope with 3D graphics rendering, a program, and a probe that fits over one finger like a finger bandage.

When the scientist gets to a bump on the surface he or she feels it. In this way scientists can feels surfaces. They have even felt viruses. A multipurpose nanomanipulator has been built to perform nanomanipulation studies under vacuum inside a scanning electron microscope as well. It can also be used to build simple objects and may eventually allow the operator to 'feel' when they pick up and move atoms. If this was virtually converted to fingertips, we could indeed build structures as if we build things in our everyday environment. In other words, we could use atoms as if they were really small objects for building, like Lego brick. Specific devieces for picking up atoms have already been invented and are called nanotweezers. Using nanotweezers is a bit like picking up Lego bricks with chopsticks.

4.1.4.2. Nanotweezers

Two researchers at Harvard University have created a nanoscale grasping device ideal for measuring and manipulating molecular structures. The device is used with the scanning probe microscope and consists of carbon nanotubes tips to form tweezer-like structures. The tweezer structure can be closed with an applied electrical field like the pair of chopsticks to produce a device that grasps and move molecules or atoms. Nanotubes are specific carbon structures that grow to create hollow tubes only one or two nanometers in diameter. The tubes are mechanically robust and are also good conductor of electricity, making them ideal for scanning probe techniques. In nanotweezers, nanotubes are connected to a gold electrode. An even finer version of the device is being researched, where the narrowest possible tubes would be directly grown on the gold electrodes using vapour deposition, called chemical vapour deposition or CVD. However, even with the finest carbon nanotubes the tips are quite crude. The design of tips for the SPM that incorporate individual molecules specifically synthesized for the purpose of lifting atoms is a likely next step, and one that seems essential if we are to make progress in using SPMs to guide chemical reactions in a selective way. Nevertheless, quite a few structures have already been built using the current primitive technology. These include corrals to hold electrons and structures with missing atoms.

The hybrid nanorobotic manipulation system integrates a TEM nanorobotic manipulator (TEM manipulator) into an SEM nanorobotic manipulator (SEM manipulator).

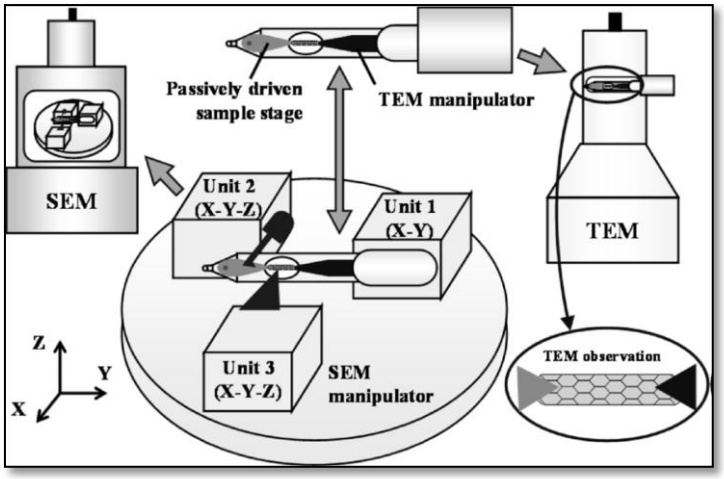


Figure-1.81.shows the schematic diagram of the hybrid nanorobotic manipulations system.

The TEM manipulator can be set inside an SEM and a TEM for sample preparation. It is also mounted a passively driven sample stage. The stage is premanipulated by the SEM manipulator for sample preparations inside the SEM. The methodology is named the hybrid nanorobotic manipulation so as to differentiate it from those with only an exchangeable specimen holder. This system can realize an efficient sample preparation with a sufficiently wide working space of SEM manipulators and sufficiently high resolution to identify nanoscale objects with a TEM. Their specifications are listed in **Table-1.13**. The resolution of H-800 is ten times higher than that of JSM-6500F; it is of subnano order. On the other hand, the observation space of JSM-6500F is approximately 10 000 times larger than that of H-800. Hence, TEM is well suited to measure and evaluate nanoscale objects, and SEM is preferred for setting manipulators and samples for efficient sample preparation.

Electron Microscope	TEM (Hitachi, H-800)	FE-SEM (JEOL, JSM-6500F)
Acceleration Voltage	35-200KV	0.5-30KV
Magnification	x 1,000 ~ x 600,000	x10~x500,000
Resolution	0.24nm (Lattice interval) 0.45nm (point-point interval)	1.5nm
Observation Space	ϕ2mm x ± 0.3mm	70mm x 50mm x 3- 40mm

Table-1.13.Specifications of FE-SEM (JSM-6500F) andTEM (H-800)

A. Passively Driven TEM Sample Stage

The space of a TEM sample chamber is quite narrow and strictly limited due to the principle of a TEM, which includes a high vacuum environment, short distance between an upper and a lower polepiece, short working distance, and so on. These space limitations cause the difficulty of constructing multi-DOF manipulation systems inside a TEM sample chamber.

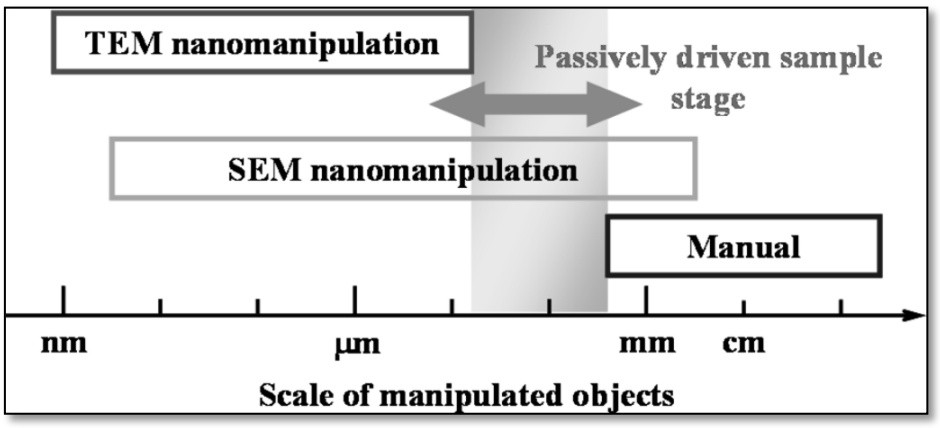


Figure-1.82.shows the scale of manipulated objects through SEM and TEM manipulations.

The working space of a TEM manipulator is also much smaller than that of an SEM manipulator with normally used actuators. If the actuation mechanism is installed in the outside of a sample chamber, it has a high cost and is limited at the reconstruction of a TEM. On the other hand, manual adjustment can be reached only from the positioning resolution of a sample. Hence, it is difficult to adjust the position of a sample within the working area of the TEM manipulator manually. Here, we propose a sample stage passively driven by SEM nanorobotic manipulators for coarse positioning adjustment of TEM samples.

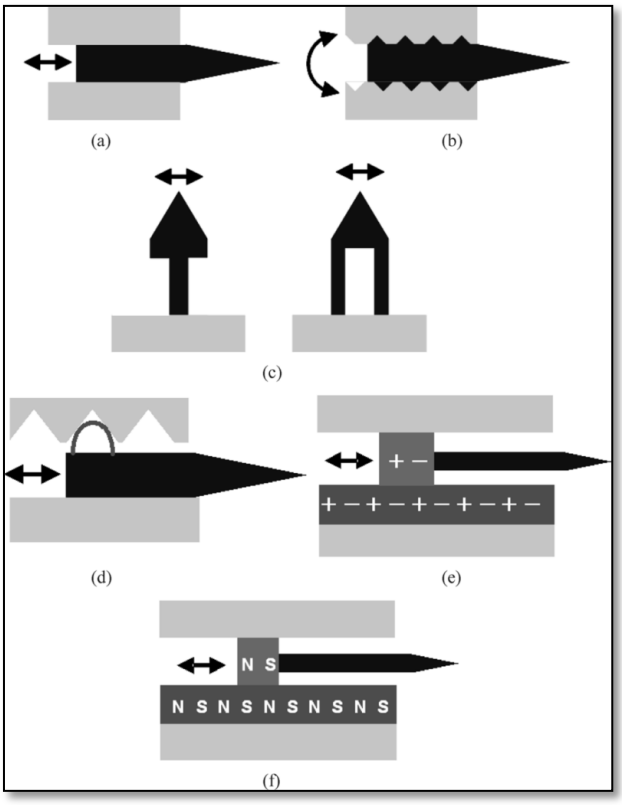


Figure-1.83.Classification of the passive driven mechanism is given here and shown in Fig. 5: (a) friction type, (b) screw type, (c) plastic deformation type, (d) elastic deformation type, (e) electrostatic type, and (f) magnetic force type.

Types (a)–(c) are relatively easy to be constructed and used as disposable. Types (d)–(f) have relatively high endurance; however, their complex mecha nisms are not easy to be constructed with a sufficiently high positioning resolution

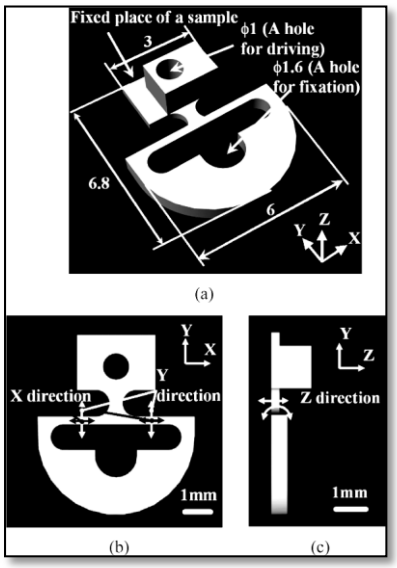


Figure-1.84.shows the schematic diagram of a constructed passively driven sample stage. Samples are fixed at the tip of the sample stage.

The sample stage has two holes; one is used for driving by SEM manipulators and the other is used for fixation on a TEM sample holder. The two thin beams and a plate are driven in the and -directions, for the -direction by bent of two beams **[see Figure-1.84 (b)]**, for the -direction by tensile and compressive bent of two beams **[see Figure-1.84 (b)],** and for the – directions by twist bent of a plate and beams **[see Figure-1.84 (c)].**

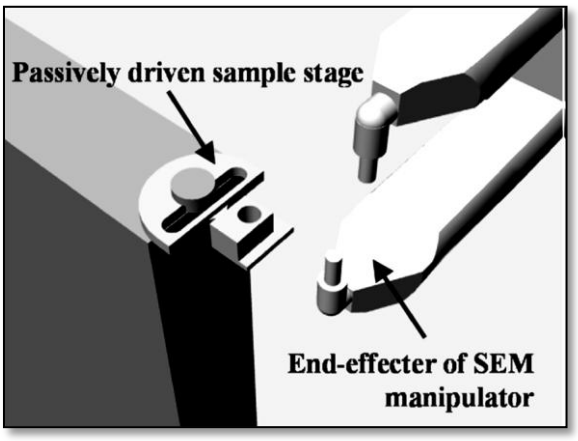


Figure-1.85.shows the configuration of a passively driven sample stage and an end-effecter of the SEM manipulator

To avoid the magnetic field produced by processing, a nonmagnetic metal is needed. We have always used aluminium.however, a relatively large elastic deformation is not suitable for precise operation, and this causes the error of the stage movement at plastic deformation.

B. TEM Nanorobotic Manipulation System

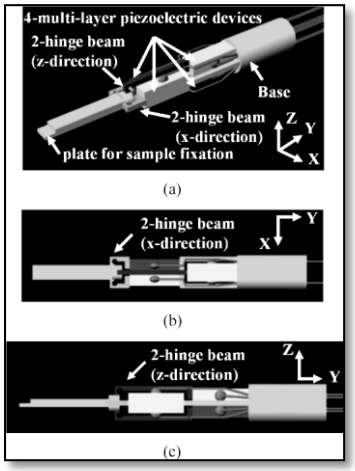


Figure-1.86.shows the 3-D schematic diagram of the TEM nanomanipulator.

consists of four multilayer piezoelectric devices, two two-hinge beams, a plate for sample fixation, and a base. All parts are made of aluminum to avoid the magnetic field produced by processing. The two hinge beams are used for the_translational movements in the - and - directions, as shown in **Figure-1.86 (b) and (c).**

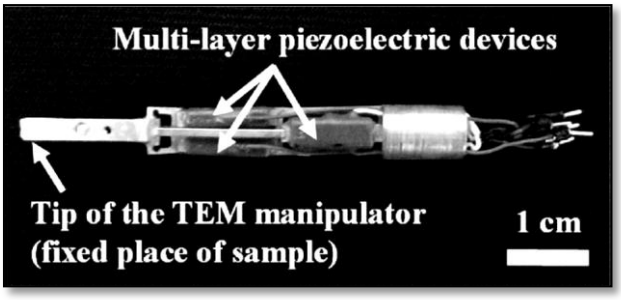


Figure-1.87.shows the overview of the constructed TEM nanomanipulator.

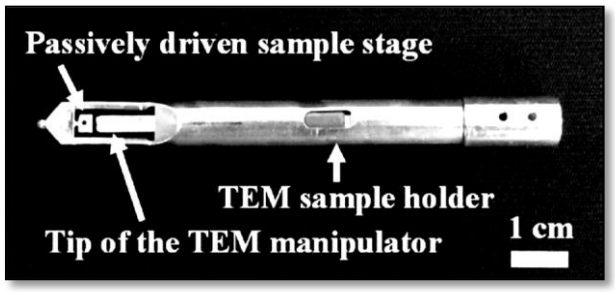


Figure-1.88.shows the TEM manipulator can be installed inside a normal-type side-entry TEM sample holder, which has an inner diameter of 7 mm.

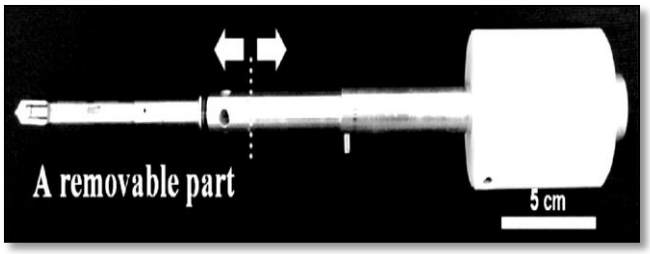


Figure-1.89.It is set on the side-entry-type TEM sample holder, as shown in Figure-1.88. The tip part is able to be removed for setting on the SEM manipulator.

C. SEM Nanorobotic Manipulation System

The SEM manipulators have been constructed with a maximum of 16 DOF with four units . The characteristics of SEM manipulators include a sufficiently wide working space and multiprobes with multiunits for preparing samples.. The overview of SEM manipulator is shown in **Figure-1.90**

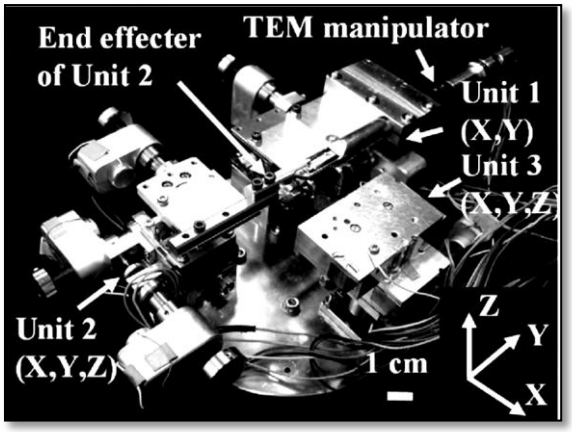


Figure-1.90.A gas introduction system is equipped on the SEM,

It can be readily used for nanofabrication.Unit 1 is used for driving the TEM manipulator and the fixation of samples. Unit 2 is used for driving the passive sample stage of the TEM manipulator, Unit 3 is used for the fixation of samples.

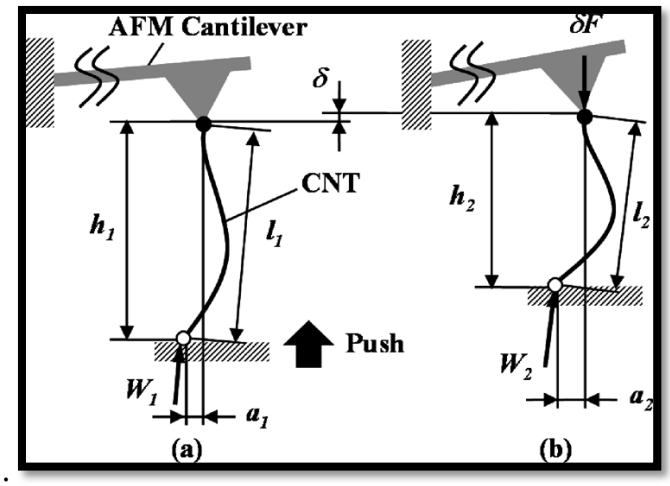


Figure-1.91.In situ measurement of young's modulus of a cnt inside the tem

To demonstrate the effectiveness of the hybrid nanorobotic manipulation system, the elasticity of an MWCNT is measured inside a TEM with in situ force measurement using an AFM cantilever.

4.1.4.3. Nanorobots

Nanorobots are nanodevices that will be used for the purpose of maintaining and protecting the human body against pathogens. They will have a diameter of about 0.5 to 3 microns and will be constructed out of parts with dimensions in the range of 1 to 100 nanometers. The main element used will be carbon in the form of diamond / fullerene nanocomposites because of the strength and chemical inertness of these forms. Many other light elements such as oxygen and nitrogen can be used for special purposes. To avoid being attacked by the host's immune system, the best choice for the exterior coating is a passive diamond coating. The smoother and more flawless the coating, the less the reaction from the body's immune system. Such devices have been designed in recent years but no working model has been built

so far. The powering of the nanorobots can be done by metabolising local glucose and oxygen for energy. In a clinical environment, another option would be externally supplied acoustic energy. Other sources of energy within the body can also be used to supply the necessary energy for the devices. They will have simple onboard computers capable of performing around 1000 or fewer computations per second. This is because their computing needs are simple. Communication with the device can be achieved by broadcast-type acoustic signalling. A navigational network may be installed in the body, with stationkeeping navigational elements providing high positional accuracy to all passing nanorobots that interrogate them, wanting to know their location. This will enable the physician to keep track of the various devices in the body. These nanorobots will be able to distinguish between different cell types by checking their surface antigens (they are different for each type of cell). This is accomplished by the use of chemotactic sensors keyed to the specific antigens on the target cells. When the task of the nanorobots is completed, they can be retrieved by allowing them to exfuse themselves via the usual human excretory channels. They can also be removed by active scavenger systems. This feature is design-dependent.

4.1.5. Importance for AFM

A key application of NEMS is atomic force microscope tips. The increased sensitivity achieved by NEMS leads to smaller and more efficient sensors to detect stresses, vibrations, forces at the atomic level, and chemical signals. **[70]** AFM tips and other detection at the nanoscale rely heavily on NEMS. If implementation of better scanning devices becomes available, all of nanoscience could benefit from AFM tips.

4.1.6. Approaches to miniaturization

Two complementary approaches to fabrication of NEMS systems can be found. The top-down approach uses the traditional micro fabrication methods, i.e. optical and electron beam lithography, to manufacture devices. While being limited by the resolution of these methods, it allows a large degree of control over the resulting structures. Typically, devices are fabricated from metallic thin films or etched semiconductor layers. Bottom-up approaches, in contrast, use the chemical properties of single molecules to cause single-molecule components to (a) self-organize or self-assemble into some useful conformation, or (b) rely on positional assembly. These approaches utilize the concepts of molecular self-assembly and/or molecular recognition. This allows fabrication of much smaller structures, albeit often at the cost of limited control of the fabrication process. A combination of these approaches may also be used, in which nanoscale molecules are integrated into a top-down framework. One such example is the carbon Nanotube nanometre.

4.1.7. Difficulties

Despite all of the useful properties of carbon nanotubes and graphene for NEMS technology, both of these products face several hindrances to their implementation. One of the main problems is carbon's response to real life environments. Carbon nanotubes exhibit a large change in electronic properties when exposed to oxygen. **[77]** Similarly, other changes to the electronic and mechanical attributes of carbon based materials must fully be explored before their implementation, especially because of their high surface area which can easily react with surrounding environments. Carbon Nanotubes were also found to have varying conductivities, being either metallic or semiconducting depending on their helicity when

processed. [78] Because of this, very special treatment must be given to the nanotubes during processing, in order to assure that all of the nanotubes have appropriate conductivities. Graphene also has very complicated electric conductivity properties compared to traditional semiconductors as it lacks an energy band gap and essentially changes all the rules for how electrons move through a graphene based device.[75] This means that traditional constructions of electronic devices will likely not work and completely new architectures must be designed for these new electronic devices.

4.1.8. Simulations

Computer simulations have long been important counterparts to experimental studies of NEMS devices. Through continuum mechanics and molecular dynamics (MD), important behaviors of NEMS devices can be predicted via computational modelling before engaging in experiments. [79-81] Additionally, combining continuum and MD techniques enables engineers to efficiently analyze the stability of NEMS devices without resorting to ultra-fine meshes and time-intensive simulations.[79] Simulations have other advantages as well: they do not require the time and expertise associated with fabricating NEMS devices; they can effectively predict the interrelated roles of various electromechanical effects; and parametric studies can be conducted fairly readily as compared with experimental approaches. For example, computational studies have predicted the charge distributions and "pull-in" electromechanical responses of NEMS devices. [82-84] Using simulations to predict mechanical and electrical behaviour of these devices can help optimize NEMS device design parameters.

4.1.9. Future of NEMS

Before NEMS devices can actually be implemented, reasonable integrations of carbon based products must be created. The focus is currently shifting from experimental work towards practical applications and device structures that will implement and profit from the use of carbon nanotubes [72] At this point in NEMS research, there is a general understanding of the properties of carbon nanotubes and graphene. The next challenge to overcome involves understanding all of the properties of these carbon based tools, and using the properties to make efficient and durable NEMS with low failure rate [84] NEMS devices, if implemented into everyday technologies, could further reduce the size of modern devices and allow for better performing sensors. Carbon based materials have served as prime materials for NEMS use, because of their highlighted mechanical and electrical properties. Once NEMS interactions with outside environments are integrated with effective designs, they will likely become useful products to everyday technologies. A graphene varactor has been fabricated which operates passively for radiation dosimeter applications.

CHAPTER-2

LITERATURE REVIEW

2.1. Litearture Reveiw of Nanotechnology

Nanotechnology raises many of the same issues as any new technology, including concerns about the toxicity and environmental impact of nanomaterial **[1]** and their potential effects on global economics, as well as speculation about various doomsday scenarios. These concerns have led to a debate among advocacy groups and governments on whether special regulation of nanotechnology is warranted.The scanning tunnelling microscope, an instrument for imaging surfaces at the atomic level, was developed in 1981 by Gerd Binnig and Heinrich Rohrer at IBM Zurich Research Laboratory, for which they received the Nobel Prize in Physics in 1986 **[2]** Fullerenes were discovered in 1985 by Harry Kroto, Richard Smalley, and Robert Curl, who together won the 1996 Nobel Prize in Chemistry **[3. 4]** Around the same time, K. Eric Drexler developed and popularized the concept of nanotechnology and founded the field of molecular nanotechnology. In the early 2000s, the field was subject to growing public awareness and controversy, with prominent debates about both its potential implications, exemplified by the Royal Society's report on nanotechnology, **[5]** as well as the feasibility of the applications envisioned by advocates of molecular nanotechnology, which culminated in the public debate between Eric Drexler and Richard Smalley in 2001 and 2003. **[6].** The early 2000s also saw the beginnings of commercial applications of nanotechnology, although these were limited to bulk applications of nanomaterial, such as the Silver Nano platform for using silver nanoparticles as an antibacterial agent, nanoparticle-based transparent sunscreens, and carbon nanotubes for stain-resistant textiles **[7].** By convention, nanotechnology is taken as the scale range 1 to 100 nm following the definition used by the National Nanotechnology Initiative in the US. The lower limit is set by the size of atoms (hydrogen has the smallest atoms, which are approximately a quarter of an nm diameter) since nanotechnology must build its devices from atoms and molecules. The upper limit is more or less arbitrary but is around the size that phenomena not observed in larger structures start to become apparent and can be made use of in the nano device**.[8]** These new phenomena make nanotechnology distinct from devices which are merely miniaturised versions of an equivalent macroscopic device; such devices are on a larger scale and come under the description of micro technology**.[9]** To put that scale in another context, the comparative size of a nanometre to a meter is the same as that of a marble to the size of the earth**.[10]** Or another way of putting it: a nanometre is the amount an average man's beard grows in the time it takes him to raise the razor to his face **[10]**.Two main approaches are used in nanotechnology. In the "bottom-up" approach, materials and devices are built from molecular components which assemble themselves chemically by principles of molecular recognition. In the "top-down" approach, nano-objects are constructed from larger entities without atomic-level control **[11]**. Much of the fascination with nanotechnology stems from these quantum and surface phenomena that matter exhibits at the nanoscale**. [12]** DNA tetrahedron **[15]** is an artificially designed nanostructure of the type made in the field of DNA nanotechnology. Each edge of the tetrahedron is a 20 base pair DNA double helix, and each vertex is a three-arm junction. Approaches from the field of "classical" chemical synthesis (inorganic and organic synthesis) also aim at designing molecules with well-defined shape, e.g. bis-peptides **[17].** Bio nanotechnology is the use of bio molecules for applications in nanotechnology, including use of viruses. **[19]** According to Be rube, there may be a danger that a "nano bubble" will form, or is forming already, from the use of the term by scientists

and entrepreneurs to garner funding, regardless of interest in the transformative possibilities of more ambitious and far-sighted work. **[29]** Researchers have discovered that bacteriostatic silver nanoparticles used in socks to reduce foot odor are being released in the wash. These particles are then flushed into the waste water stream and may destroy bacteria which are critical components of natural ecosystems, farms, and waste treatment processes **[30].** Public deliberations on risk perception in the US and UK carried out by the Centre for Nanotechnology in Society found that participants were more positive about nanotechnologies for energy applications than for health applications, with health applications raising moral and ethical dilemmas such as cost and availability. **[31]** Experts, including director of the Woodrow Wilson Centre's Project on Emerging Nanotechnologies David Rejeski, have testified **[32]** that successful commercialization depends on adequate oversight, risk research strategy, and public engagement. Berkeley, California is currently the only city in the United States to regulate nanotechnology**.** Cambridge, Massachusetts in 2008 considered enacting a similar law, **[33]** but ultimately rejected it. **[34]** Relevant for both research on and application of nanotechnologies, the insurability of nanotechnology is contested. **[35]** Researchers have found that when rats breathed in nanoparticles, the particles settled in the brain and lungs, which led to significant increases in biomarkers for inflammation and stress response and those nanoparticles, induce skin aging through oxidative stress in hairless mice **[36, 37].** A two-year study at UCLA's School of Public Health found lab mice consuming nano-titanium dioxide showed DNA and chromosome damage to a degree "linked to all the big killers of man, namely cancer, heart disease, neurological disease and aging".**[38].** Anthony Seaton of the Institute of Occupational Medicine in Edinburgh, Scotland, who contributed to the article on carbon nanotubes, said "We know that some of them probably have the potential to cause mesothelioma. So those sorts of materials need to be handled very carefully." **[39]** In the absence of specific regulation forthcoming from governments, Paull and Lyons (2008) have called for an exclusion of engineered nanoparticles in food. **[40]** A newspaper article reports that workers in a paint factory developed serious lung disease and nanoparticles were found in their lungs**.** **[41]** Calls for tighter regulation of nanotechnology have occurred alongside a growing debate related to the human health and safety risks of nanotechnology. **[42]** There is significant debate about who is responsible for the regulation of nanotechnology. Some regulatory agencies currently cover some nanotechnology products and processes (to varying degrees) – by "bolting on" nanotechnology to existing regulations – there are clear gaps in these regimes. **[43]** Davies (2008) has proposed a regulatory road map describing steps to deal with these shortcomings. **[44].** Stakeholders concerned by the lack of a regulatory framework to assess and control risks associated with the release of nanoparticles and nanotubes have drawn parallels with bovine spongiform encephalopathy ("mad cow" disease), thalidomide, genetically modified food, **[45]** nuclear energy, reproductive technologies, biotechnology, and asbestosis. Dr. Andrew Maynard, chief science advisor to the Woodrow Wilson Centre's Project on Emerging Nanotechnologies, concludes that there is insufficient funding for human health and safety research, and as a result there is currently limited understanding of the human health and safety risks associated with nanotechnology. **[46]** As a result, some academics have called for stricter application of the precautionary principle, with delayed marketing approval, enhanced labelling and additional safety data development requirements in relation to certain forms of nanotechnology. **[47].** researchers have combined a magnetic moiety visible on NMR with a radioisotope and a near-IR fluorescent probe, all linked to antibodies that highlight different types of diseased tissues. **[48]** Near term nanoscale approaches (albeit atomically imprecise) have yielded significant results (11% efficiency) **[49].** Nanotechnology (sometimes shortened to "nanotech") is the study of manipulating matter on an atomic and molecular scale. Generally, nanotechnology deals with developing

materials, devices, or other structures possessing at least one dimension sized from 1 to 100 nanometres. A material such as gold, which is chemically inert at normal scales, can serve as a potent chemical catalyst at nanoscales. Much of the fascination with nanotechnology stems from these quantum and surface phenomena that matter exhibits at the nanoscale. **[85]** Two main approaches are used in nanotechnology. In the "bottom-up" approach, materials and devices are built from molecular components which assemble themselves chemically by principles of molecular recognition. In the "top-down" approach, nano-objects are constructed from larger entities without atomic-level control. Nanotechnology is considered a key technology for the future. Nanotechnology entails the application of fields of science as diverse as surface science, organic chemistry, molecular biology, semiconductor physics, micro-fabrication, etc. Nanotechnology distinct from devices which are merely miniaturized versions of an equivalent macroscopic device; such devices are on a larger scale and come under the description of micro technology. It is hoped that developments in nanotechnology will make possible their construction by some other means, perhaps using bio mimetic principles. However, Drexler and other researchers have proposed that advanced nanotechnology, although perhaps initially implemented by bio mimetic means, ultimately could be based on mechanical engineering principles, namely, a manufacturing technology based on the mechanical functionality of these components (such as gears, bearings, motors, and structural members) that would enable programmable, positional assembly to atomic specification**.** **[86]** Scientists debate the future implications of nanotechnology. Nanotechnology may be able to create many new materials and devices with a vast range of applications, such as in medicine, electronics, biomaterials and energy production. On the other hand, nanotechnology raises many of the same issues as any new technology, including concerns about the toxicity and environmental impact of nanomaterial. The scanning tunnelling microscope, an instrument for imaging surfaces at the atomic level **[87].**The nanomaterial field includes subfields which develop or study materials having unique properties arising from their nanoscale dimensions. **[88]** Many technologies that 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 magneto resistance-based hard drives already on the market fit this description, Nanorobotics centres on self-sufficient machines of some functionality operating at the nanoscale. There are hopes for applying nanorobots in medicine, **[89-91]** but it may not be easy to do such a thing because of several drawbacks of such devices. **[92]** Nevertheless, progress on innovative materials and methodologies has been demonstrated with some patents granted about new nanomanufacturing devices for future commercial applications, which also progressively helps in the development towards nanorobots with the use of embedded nanobioelectronics concepts. **[93, 94]** There are several important modern developments. The atomic force microscope (AFM) and the Scanning Tunnelling Microscope (STM) are two early versions of scanning probes that launched nanotechnology The tip of a scanning probe can also be used to manipulate nanostructures (a process called positional assembly). Feature-oriented scanning methodology suggested by Rostislav Lapshin appears to be a promising way to implement these nanomanipulations in automatic mode. **[95,96]** Another group of nanotechnological techniques include those used for fabrication of nanotubes and nanowires, those used in semiconductor fabrication such as deep ultraviolet lithography, electron beam lithography etc techniques such as those employing di-block copolymers. Cars are being manufactured with nanomaterial so they may need fewer metals and less fuel to operate in the future. Most applications are limited to the use of "first generation" passive nanomaterial which includes titanium dioxide in sunscreen, cosmetics, surface coatings, **[97]** and some food products; Carbon allotropes used to produce gecko tape; silver in food packaging, clothing, disinfectants and household appliances; zinc oxide in

sunscreens and cosmetics, surface coatings, paints and outdoor furniture varnishes; and cerium oxide as a fuel catalyst.

2.1.1. Gaps in Research

1. Nanotechnology raises many of the same issues as any new technology, including concerns about the toxicity and environmental impact of nanomaterial and their potential effects on global economics, as well as speculation about various doomsday scenarios.
2. According to Be rube, there may be a danger that a "nano bubble" will form, or is forming already, from the use of the term by scientists and entrepreneurs to garner funding, regardless of interest in the transformative possibilities of more ambitious and far-sighted work.
3. Researchers have discovered that bacteriostatic silver nanoparticles used in socks to reduce foot odor are being released in the wash. These particles are then flushed into the waste water stream and may destroy bacteria which are critical components of natural ecosystems, farms, and waste treatment processes.
4. Researchers have found that when rats breathed in nanoparticles, the particles settled in the brain and lungs, which led to significant increases in biomarkers for inflammation and stress response and those nanoparticles, induce skin aging through oxidative stress in hairless mice. Stakeholders concerned by the lack of a regulatory framework to assess and control risks associated with the release of nanoparticles and nanotubes have drawn parallels with bovine spongiform encephalopathy ("mad cow" disease), thalidomide, genetically modified food,nuclear energy, reproductive technologies, biotechnology, and asbestosis. It is hoped that developments in nanotechnology will make possible their construction by some other means, perhaps using bio mimetic principles.
5. There are hopes for applying nanorobots in medicine, but it may not be easy to do such a thing because of several drawbacks of such devices.
6. Techniques such as electron beam lithography, X-ray lithography and ion beam lithography, all have advantages in terms of resolution achieved, however, there are disadvantages associated with cost, optics and detrimental effects on the substrate. These methods are currently under investigation to improve upon current lithography process used in the IC industry. Currently, the physical properties are still being discovered and disputed.
7. What makes it so difficult is that nanotubes have a very broad range of electronic, thermal and structural properties that change depending on the different kinds of nanotubes (defined by its diameter, length and chirality, or twist). To make things more interesting besides having a single cylindrical wall (SWNTs), nanotubes can have multiple walls (MWNTs) – cylinders inside the order cylinders.
8. Tools, templates and processes are currently being development that will enable high volume manufacturing of components and structures on a development of commercial products and enable the creations of a new generation of applications in various different commercial sectors including drug delivery, cosmetics, biomedical implants, electronics, and optical components, automotive and aerospace parts.
9. Molecular nanotechnology is a proposed approach which involves manipulating single molecules in finely controlled, deterministic ways. This is more theoretical than the other subfields and is beyond current capabilities. Mechanical properties of nanosystems are of interest in the nanomechanics research.
10. Nevertheless, there are many examples of self-assembly based on molecular recognition in biology, most notably Watson–Crick base pairing and enzyme-substrate interactions. The challenge for nanotechnology is whether these principles can be used to engineer

new constructs in addition to natural ones. In general it is very difficult to assemble devices on the atomic scale, as all one has to position atoms on other atoms of comparable size and stickiness. Another view, put forth by Carlo Montemagno, is that future nanosystems will be hybrids of silicon technology and biological molecular machines. Yet another view, put forward by the late Richard Smalley, is that mechanosynthesis is impossible due to the difficulties in mechanically manipulating individual molecules.

11. The detailed shape of the scanning tip is sometimes difficult to determine. Its effect on the resulting data is particularly noticeable if the specimen varies greatly in height over lateral distances of 10 nm or less. Scanning probe microscopy is often not useful for examining buried solid-solid or liquid-liquid interfaces.
12. In newer more advanced versions, currents can even be passed through the tip to probe the electrical conductivity or transport of the underlying surface, but this is much more challenging with very few research groups reporting reliable data. In micro- and nanofabrication we mean pattern transfer.
13. Owing to limitations in current photolithographic processes, there is a challenge to develop novel lithographic processes with better resolution for smaller features. where protein-based devices remain a great challenge to modelling, but not to fabrication.
14. The availability of both self-assembly and directed (mechanical, programmable) approaches at the nanoscale for the generation of new materials or complex systems provides both considerable flexibility in possible fabrication routes and considerable challenges for computational modelling and design techniques.
15. Nanostructures and nanoscale devices often challenge our ability to study matter by atomistic (both classical and quantum chemical) methods. The challenges of large, atomistic models can be enormous even in classical approximations, as shown by the scale of resources applied in the supercomputer and distributed computing studies of the protein fold-prediction problem.
16. Nanoscale science presents new challenges to both experimentalists and theoreticians. characterization is often the bottleneck in design cycles for both DNA and protein engineering. Some of these challenges could be addressed by improvements in the capabilities and the availability of cryoelectron tomography instruments.
17. The main challenge associated with computational modeling of bionanosystems is the size of the system that can be efficiently simulated. In ambient conditions, most samples develop a liquid meniscus layer. Because of this, keeping the probe tip close enough to the sample for short-range forces to become detectable while preventing the tip from sticking to the surface presents a major problem for non-contact dynamic mode in ambient conditions.
18. Problems with the AFM technique include no direct measurement of the tip-sample separation and the common need for low stiffness cantilevers which tend to 'snap' to the surface.
19. Poor vacuum in a TEM can cause several problems, from deposition of gas inside the TEM onto the specimen as it is being viewed through a process known as electron beam induced deposition, or in more severe cases damage to the cathode from an electrical discharge. Vacuum problems due to specimen sublimation are limited by the use of a cold trap to adsorb sublimated gases in the vicinity of the specimen.
20. The challenges of large, atomistic models can be enormous even in classical approximations, as shown by the scale of resources applied in the supercomputer and distributed computing studies of the protein fold-prediction problem.
21. No one has develop an integrated systems model for the structure of the nanotechnology system in terms of its constituents and interactions between the constituents and processes

2.2. Literature Reveiw of Nanomaterial based on Attributes

The nanomaterial field includes subfields which develop or study materials having unique properties arising from their nanoscale dimensions. **[16]** Nevertheless, progress on innovative materials and methodologies has been demonstrated with some patents granted about new nanomanufacturing devices for future commercial applications, which also progressively helps in the development towards nanorobots with the use of embedded nanobioelectronics concepts**. [24, 25]** Most applications are limited to the use of "first generation" passive nanomaterial which includes titanium dioxide in sunscreen, cosmetics, surface coatings, **[28]** and some food products. Further applications which require actual manipulation or arrangement of nanoscale components await further research. Though technologies branded with the term 'nano' are sometimes little related to and fall far short of the most ambitious and transformative technological goals of the sort in molecular manufacturing proposals, the term still connotes such ideas. A large number of employees are already being exposed to nanomaterial, both in research laboratories, production facilities or downstream user companies. P. Avouris et al. **[98]** have demonstrated fabricated single and multiple CNT transistors by electron beam lithography. C. Dekker et al. **[99]** have also integrated to multiple transistors to form simple logic circuits by electron beam lithography. Lourie and Wagner **[100]** have used a bar model in their experiments in which micro Raman spectroscopy were used to measure the compressive response. Yu et al. have performed direct tensile loading tests of SWCN T **[101]** K. Yamamoto et al. have pioneered the work in the electric field assist manipulation of CNT bundles. **[102][103]** Huxtable et al. **[104].** The MD simulation conducted by Shenogin **[105]** has showed that the thermal interface resistance is one of the influencing factors for the thermal conductivity of carbon-nanotube polymer composites and organic suspensions. . X.L. Chen et.al. **[106]** Have conducted finite element analysis for determining effective mechanical properties of CNT based nanocomposites using square representative volume element. Changxin Chen et al. **[107]** have reported large-scale synthesis of carbon nanotubes (CNTs) under normal temperature and pressure, using pulsed laser ablation of a graphite target in metal nano-sol. A phosphorus nickel-carbon nanotube (Ni-P-CNT) nanocomposites film is synthesized by Shen, Guang-Ren et al. **[108]** for micro electromechanical systems device fabrication. Nanoindentation measurement indicates that the Young's modulus and hardness of the Ni-P-CNT nanocomposite film plated in the bath with 0.028-g/L CNTs can greatly increase up to 665.9 and 28.9 Gap. Carbon nanotube/poly (p-phenylene benzobisoxazole) (CNT/PBO) composite fibers were prepared by in situ polymerization and dry-jet wet spinning by Li, Jinhuan **[109]** the thermal resistance of the CNT (2 wt%)/PBO fibers was reported to be higher along with the increase in tensile strength by 20-50%. CNTs/Fe/Al2O3 nanocomposites were prepared by Yoo, S.-H. et al**. [110]** using the thermal CVD and SPS methods. Price et al. have coated such tubes with metallic copper (to improve their mechanical strength) and then loaded antibiotics used to prevent marine fouling into these tubes **[111].** Rendtorff N.M. et al. **[112]** have studied the influence of the different phase content and distribution for zircon-mullite composites with 15 – 45% mullite on physical properties and thermal shock resistance. The composites were subjected to an abrasive wear test under loads of 0.1 – 2.0N with a ball-on-disc apparatus. In previous demonstrations by Taktar S. et al. **[113]** friction and wear behaviour of alumina and alumina/ mullite composites, coupled with WC-6%Co ball, were investigated using a ball-on-disc apparatus at different sliding speed and load... Rezaie H.R. et al. **[114]** have carried out a comparative study on mullite and SiC platelets-mullite composites using mullite derived from kaolinite mixed with _-alumina, and form sol-gel processing of boehmite and colloidal silica precursors. Epoxies are highly cross-linked thermosetting polymers that are increasingly being used in high performance structural applications (Bakis et al. 2002 **[115]** Compared to

other polymers, epoxies offer high strength, Young's modulus and hardness coupled with good corrosion resistance and high glass transition temperature. (Kusaka et al. 1998 **[116]** Argon and Cohen 2003 **[117].** Pearson and Yee 1989 **[118]** which limits their reliability and operating life. Consequently, there is great interest in enhancing the fracture and fatigue properties of epoxy polymers using nano filler reinforcement. A comprehensive and recent review on fullerene toxicity is given by Kolosnjaj et al. (2007a,b, c).**[119]** These authors review the works on fullerene toxicity beginning in the early 1990s to present, and conclude that very little evidence gathered since the discovery of fullerenes indicate that C_{60} is toxic. Haddon et al. **[120]** have found that intercalation of alkali-metal atoms in solid C_{60} leads to metallic behaviour. **[121]** In 1991, it was revealed that potassium-doped C_{60} becomes superconducting at 18 K. **[122]** this was the highest transition temperature for a molecular superconductor. Since then, superconductivity has been reported in fullerene doped with various other alkali metals**. [123][124]** Recently, superconductivity at 38 K has been reported in bulk Cs_3C_{60}, **[125]** but only under applied pressure. The highest superconducting transition temperature of 33 K at ambient pressure is reported for Cs_2RbC_{60}. **[126]**

2.2.1. Gaps in Research

1. Most applications are limited to the use of "first generation" passive nanomaterial which includes titanium dioxide in sunscreen, cosmetics, surface coatings, and some food products. Further applications which require actual manipulation or arrangement of nanoscale components await further research.
2. Though technologies branded with the term 'nano' are sometimes little related to and fall far short of the most ambitious and transformative technological goals of the sort in molecular manufacturing proposals, the term still connotes such ideas.
3. Fracture and fatigue properties of epoxy polymers using nano filler reinforcement.
4. High-yield production of nitride cluster fullerenes
5. It was concluded that FS of LaB6 consists of interconnecting ellipsoids at X points and thin necks [3] along C lines in the simple cubic Brillouin zone. Whereas, no band calculation has succeeded in realization such very slender necks.
6. Currently, one of the most pressing challenges facing human society is the need to find alternative energy sources due to the dwindling fossil fuel supplies as well as the detrimental impact to the environment the burning of said fuels is having.
7. The most challenging of those three areas is finding a practical method of hydrogen storage.
8. Emission properties of LaB6 with grain sizes less than 100nm of full densification. the causes of the thickness and length variations among the nanowires are still unknown, and a detailed growth mechanism still needs further investigation.
9. Recently many researchers studied the relationship between sputtering power and roughness.
10. The researchers applied the golden nanotubes to solve the challenging biomedical problem of detecting cancer cells in the lymphatic system, which is responsible for the process of metastasis.
11. In addition. illustrated the possibility that used flagella nanotubes as templates However all of these templates were quite difficult to be separated from the Pt nanotubes and most of the nanotubes were assembled by the small Pt nanocrystal.
12. For nanoparticles made in solution, uncontrollable aggregation effects can be detrimental to many applications. Controlling the shape of the hollow nanoparticles is a great challenge

13. In this communication, many researchers demonstrate that C60 nanoparticles induce both plasticization (speeded up dynamics) and antiplasticization (slowed down dynamics) effects depending on the temperature range studied..
14. An upsurge of research activities in the physics and applications of nanostructured materials has led to more attention to electronic states and luminescence properties of nanoparticle composites.
15. Ceramic based composites are also under study with the main objective of imparting toughness to the matrix by the introduction of other constituents
16. nanotubes can be used as templates for the self-assembly of protein molecules
17. Till date illustrates a qualitative relationship between the Young's modulus of a nanotube and the amount of disorder in the atomic structure of the walls
18. A less successful development has been in the area of hydrogen storage.
19. However, little work has been done on this aspect of the optical behaviour of nanofibres and the success of this approach remains to be seen.
20. Less work has been done on the thermal behaviour of CNT,
21. Applications of nanoparticles have been of special recent research and development interest, with potential applications that include use of nanoparticles as drug (or DNA) delivery vehicles, and as components in medical diagnostic kits, biosensors and membranes for bio separations. Spherical nanoparticles are typically used for such applications,
22. The problem of heat transfer in composites filled with fibers has been extensively studied for decades.
23. Very little study has been made on the theoretically and experimentally on the conductivity of the nanotube in the transverse directions.
24. Diameter-based separation is more difficult, because differences in the physical and/or chemical properties caused by diameter changes are smaller and because variations in tube length could be a dominant factor in physical-based separation methods
25. The present way of doing literature review has so many limitations. The area of nanotechnology and their uses are spread at very fast rate day by day. So it is very difficult to derive the appropriate knowledge in the area of nanomaterial.

2.3. Literature Review of Nanomaterial Selection

Nanomaterial is those materials where the size of the individual building block is less than 100nm at least in one dimension. Nanomaterial means any intentionally produced material that has one or more dimensions of the order of 100nm or less or is composed of discrete functional parts, either internally or at the surface, many of which have one or more dimensions of the order of 100nm or less, including structures, agglomerates or aggregates, which have a size above the order of 100nm but retain properties that are characteristic to the nano-scale. Selection of the appropriate material is an integral part of successfully implementation of an engineer's design. The ability to select the most appropriate material for a given application is the fundamental challenges faced by the design engineer. A systematic and efficient approach to material selection approach is necessary in order to select the best alternative for a given application **[127, 128].**The importance of materials selection in engineering design has been well recognized. The design decision-making regarding selecting appropriate materials is dictated by the specific requirements of an application, often the requirements on materials properties **[129].**In the past lots of research had been reported for selection of material using classical multi attribute decision-making methods. A multi attribute analysis is a popular tool to select best alternative for given applications and the methods are simple additive weighted (SAW) method, weighted product method (WPM), technique for order preference by similarity to ideal solution (TOPSIS), Vlse Kriterijumska Optimizacija Kompromisno Resenje (VIKOR) method, analytical hierarchy process (AHP), graph theory and matrix representation approach (GTMA) etc. Material selection is one of the most challenging issues in the design and development of structural elements and it is critical the success and competitiveness of the manufacturing organisation. Thus, great efforts need to be extended to determine attributes that influence material selection, using a simple logical approach, to eliminate unsuitable materials and selection of a proper material to be strengthen the existing material selection procedure. The selection of an optimal material for an engineering design from among various alternatives based on different attributes (i.e. subjective, objective) is defined within the concept of a multiple attribute decision-making (MADM) problem. There has been rapid increase in the number of nanomaterial and nanomaterial manufacturers. Nanomaterial with vastly different capabilities and specifications are available for a wide range of applications. The selection of the nanomaterial to suit a particular application and production environment, from the large number of nanomaterial available in the market today has become a difficult task. Various considerations such as availability, recycling, production method, disposal method, design life need to be considered before a suitable nanomaterial be selected. The complexity of problem is better appreciated when one realizes that there are over 125 attributes that have to be considered in the selection of nanomaterial for particular application. Moreover, many of them are conflicting in nature and have different units, which cannot be unified and compared. There are a number of reported studies concerning the selection of nanomaterial for manufacturing applications. Rao et al. **[130]** presented graph theory and matrix representation approach (GTMA) for the material selection. Shanian and Savadogo **[131]** presented Elimination and Et Choice Translating Reality (ELECTRE) outranking method for the material selection. Shanian and Savadogo **[132]** applied TOPSIS method as multiple-criteria decision support analysis for material selection of metallic bipolar plates for polymer electrolyte fuel cell. Manshadi et al. **[133]** proposed numerical method for the material selection combining non-linear normalization with modified digital logic method. Chan and Tong **[134]** used grey relational analysis approach (GRA) for multi-criteria selection method. Rao **[135]** presented improved compromise ranking method for material selection. Rao and Davim **[136]** described combined multiple attribute decision-making AHP/TOPSIS

methodology. Prasenjit et al**. [137]** used compromise ranking and outranking methods for material selection. Material selection is carried out using fuzzy decision-making, material design and selection using multi objective decision-making methods **[138-141].** PSI method for material selection, with one example in consideration had already been solved using improved compromise ranking method by Rao. Rao and Davim **[142]** proposed a logical procedure which is based on a combined technique for order preference by similarity to ideal solution (TOPSIS) and analytical hierarchy process (AHP) method for material selection problem in engineering design. Shanian and Savadogo **[143,144]** presented a material selection model using a MADM (Multiple Attribute Decision Making) method known as ELECTRE. Rao **[145]** developed material selection methodology using an improved compromise ranking method, also known as VIKOR. Wang and Chang **[146]** emphasized a fuzzy multiple criteria decision-making approach to help selecting the best suited tool steel material for a specific manufacturing application. Liao **[147]** took the advantage of a fuzzy multi-criteria decision-making method for material selection. Even though a good amount of research work was conducted in the past on materials selection, there is a need for a model selection interface to guide practitioners/researchers in matching suitable MADM methods with the material selection decision under different circumstances. Suresh Babu et al. **[148]** have presented an illustrative problem for the material selection for typical wind turbine blades using TOPSIS (Technique for Order Preference by Similarity to Ideal Solution) method. The pertinent attributes identified were less and more emphasis has been given to put forward TOPSIS methodology applied to nanomaterial selection.

2.3.1. Gaps in Research

3. The ability to select the most appropriate nanomaterial for a given application is the fundamental challenges faced by the design engineer.
4. Nanomaterial selection is one of the most challenging issues in the design and development of structural elements and it is critical the success and competitiveness of the manufacturing organisation.
5. Moreover, many of the nanomaterial attribute for their selection are conflicting in nature and have different units, which cannot be unified and compared.
6. Pertinent attributes identified were less and more emphasis has been given to put forward TOPSIS methodology applied to nanomaterial selection.
7. Vague set is generalized form fuzzy sets, vague sets can express and deal with the uncertainty of fuzziness which contain more abundant information.
8. TOPSIS did not take account of the relative importance of the distance from each point to Positive Ideal Solution and Negative Ideal Solution.
9. For multi-criteria problem structures, it requires defining a number attributes and assigning corresponding FR values to each of them.
10. In the recent research proposals towards analytical modelling of material selection problems, the lack of a systematic way to assign suitable models along with the different cases has clearly seemed.
11. There is a need for a model selection interface to guide practitioners/researchers in matching suitable MADM methods with the material selection decision under different circumstances.
12. A systematic and efficient approach to material selection approach is necessary in order to select the best alternative for a given application.
13. A validation for any new approach is not just sufficient but it also requires checking of its consistency by applying the proposed method to other problems

14. To decide which method to apply, matching methods with classes of appropriate problems are needed.
15. The validation procedures have to be developed, and application feasibility should be explored.
16. The conceptual and operational validation of the application of a method in real world problems is needed.
17. Researchers are challenged to provide a guide for choosing the method that is both theoretically well founded and practically operational to solve actual problems.
18. No work has been contributed to developed a model selection interface to enable analytical solutions to different problem concepts in nanomaterial selection under multiple attribute decision-making (MADM) environments
19. Coding scheme and the selection procedures of nanomaterial using mathematical and graphical methods with example is not presented anywhere.

2.4. Literature Reveiw of Nanodevice

Ever growing demand of nanoactuators for high productivity includes use of various model arrangements for variety of applications designing a nanoactuator that supports converged applications require careful considerations of type of applications that the nanoactuator needs to support and the types of actuators resources theses applications require. There are a number of issues that must be considered for the nanoactuator design; some are common to all applications. Designing nanoactuator for actuation, modification, realization and performance one at a time is not time consuming but also requires various iterations as design requirements/constraints for ability considered at later stage may require revisiting design for ability already considered .Molecular scale electronics seeks to develop molecules with useful electronic properties. These could then be used as single-molecule components in a nanoelectronic device **[18].** Though biology clearly demonstrates that molecular machine systems are possible, non-biological molecular machines are today only in their infancy. Leaders in research on non-biological molecular machines are Dr. Alex Zettl and his colleagues at Lawrence Berkeley Laboratories and UC Berkeley. They have constructed at least three distinct molecular devices whose motion is controlled from the desktop with changing voltage: a nanotube nanomotor, a molecular actuator, **[13]** and a nanoelectromechanical relaxation oscillator. **[14].** Nanocellulose is a potential bulk-scale application. Nanorobotics centres on self-sufficient machines of some functionality operating at the nanoscale. There are hopes for applying nanorobots in medicine, **[20, 21, 22]** but it may not be easy to do such a thing because of several drawbacks of such devices**. [23].** Feature-oriented scanning methodology suggested by Rostislav Lapshin appears to be a promising way to implement these nanomanipulations in automatic mode. **[26, 27].** Considerable work has been done on the interfaces between molecular electronics and conventional metals, as reported by Reed and associates **[50].** For comparison, note that existing silicon photovoltaic cells can reach an efficiency of 24% (at 0 C) **[51].** MEMS devices generally range in size from 20 micrometres (20 millionths of a metre) to a millimetre (i.e. 0.02 to 1.0 mm). They usually consist of a central unit that processes data (the microprocessor) and several components that interact with the outside such as micro sensors**. [52].** An early example of a MEMS device is the resonistor – and electromechanical monolithic resonator **[53, 54]** The fabrication of MEMS evolved from the process technology in semiconductor device fabrication, i.e. the basic techniques are deposition of material layers, patterning by photolithography and etching to produce the required shapes**.[55]** AlN crystallizes in the wurtzite structure and thus shows pyroelectric and piezoelectric properties enabling sensors, for instance, with sensitivity to normal and shear forces. **[56]** TiN, on the other hand, exhibits a high electrical conductivity and large elastic modulus allowing realizing electrostatic MEMS actuation schemes with ultrathin membranes. **[57].** Electron beam lithography (often abbreviated as e-beam lithography) is the practice of scanning a beam of electrons in a patterned fashion across a surface covered with a film (called the resist), **[58]** ("exposing" the resist) and of selectively removing either exposed or non-exposed regions of the resist ("developing"). the material is sputtered or dissolved using reactive ions or a vapour phase etchant. **[59, 60]** for a somewhat dated overview of MEMS etching technologies.Los Angeles**.[61, 62]** Primarily used for releasing metal and dielectric structures by undercutting silicon, XeF_2 has the advantage of a stiction-free release unlike wet etchants. Its reaction to silicon is "plasma less", is purely chemical and spontaneous and is often operated in pulsed mode. Models of the etching action are available, **[63]** and university laboratories and various commercial tools offer solutions using this approach. The primary technology is based on the so-called "Bosch process", **[64]** named after the German company Robert Bosch, which filed the original patent, where two different gas compositions alternate in the reactor. Surface

micromachining uses layers deposited on the surface of a substrate as the structural materials, rather than using the substrate itself. **[65].** Accelerometers in consumer electronics devices such as game controllers (Nintendo Wii), personal media players / cell phones (Apple phone, various Nokia mobile phone models, various HTC PDA models) **[66]** and a number of Digital Cameras (various Canon Digital IXUS models). Also used in PCs to park the hard disk head when free-fall is detected, to prevent damage and data loss. 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 **[67]** The name derives from typical device dimensions in the nanometre range, leading to low mass, high mechanical resonance frequencies, potentially large quantum mechanical effects such as zero point motion, and a high surface-to-volume ratio useful for surface-based sensing mechanisms**.[68].** In 2000, the first very-large-scale integration (VLSI) NEMS device was demonstrated by researchers from IBM. **[69].** The increased sensitivity achieved by NEMS leads to smaller and more efficient sensors to detect stresses, vibrations, forces at the atomic level, and chemical signals. **[70].** Both graphene and carbon exhibit high Young's modulus, excessively low density, low friction and large surface area**.[71, 72]** The low friction of CNTs, allow practically frictionless bearings and has thus been a huge motivation towards practical applications of CNTs as constitutive elements in NEMS, such as nanomotors, switches, and high-frequency oscillators **[72]** Carbon nanotubes and graphene's physical strength allows carbon based materials to meet higher stress demands, when common materials would normally fail and thus further support their use as a major materials in NEMS technological development. **[73].** Along with the mechanical benefits of carbon based materials, the electrical properties of carbon nanotubes and graphene allow it to be used in many electrical components of NEMS. Nanotransistors have been developed for both carbon nanotubes **[74]** as well as graphene**. [75].** This is a very useful property as wires to transfer current are another basic building block of any electrical system. Carbon nanotubes have specifically found so much use in NEMS that methods have already been discovered to connect suspended carbon nanotubes to other nanostructures. **[76].** Carbon nanotubes exhibit a large change in electronic properties when exposed to oxygen. **[77].** Carbon Nanotubes were also found to have varying conductivities, being either metallic or semiconducting depending on their helicity when processed. **[78]** Because of this, very special treatment must be given to the nanotubes during processing, in order to assure that all of the nanotubes have appropriate conductivities. Graphene also has very complicated electric conductivity properties compared to traditional semiconductors as it lacks an energy band gap and essentially changes all the rules for how electrons move through a graphene based device**.[75].** Computer simulations have long been important counterparts to experimental studies of NEMS devices. Through continuum mechanics and molecular dynamics (MD), important behaviors of NEMS devices can be predicted via computational modelling before engaging in experiments. **[79-81].** For example, computational studies have predicted the charge distributions and "pull-in" electromechanical responses of NEMS devices. **[82-84]** Many of the research contributions have been published in the field of actuation, design, performance, positioning and realization of nanoactuator. Most of these studies focus each ability of a nanoactuator at a time. On the other hand almost all the studies published in the area of design for x-abilities and concurrent design are in the field of manufacturing, construction etc. Relatively no one has contributed in the design of nanoactuator using concurrent engineering for x-abilities, at the same time no literature is available for selection of nanoactuator elements using multi attribute decision making (MADM) approach. For the past decade nanotechnology has greatly influenced all science and engineering branches including physics **[149],** electronics **[150],** civil engineering **[151],** material engineering **[152]** etc. In the electronic world, nano-electromechanical systems (NEMS) have become the center of interest for developing ultra-small devices. There are several kinds of NEMS actuated by

electrostatic forces including flexural actuators as well as torsional actuators **[153-155].** The physical behavior of the torsional actuators has been extensively studied in micro scales **[156-161].** Many researchers contributed in the field of manufacturing and construction sector of nanodevices including nanoactuator by considering various models and physical characteristics/attributes/properties depending on various applications, some of literature review are presented here. Some researchers developed analytical lumped-mass models to simulate the pull-in performance of torsional micro mirrors **[157-159].** Nemirovsky **[162]** were the first researchers to introduce a lumped-mass model to capture the torsion/bending coupled behavior of torsional micro-actuators. With reduction of dimensions from micro to sub-micro, nano-scale effects appear. One of the most important effects that appear at nano-scale dimensions is the size dependency of material characteristics. Therefore, non-classical continuum theories such as non-local elasticity **[163],** couple stress **[164],** modified couple stress theory **[165]** and augmented continuum mechanics **[166, 167]** are proposed to interpret the size-dependent behavior of nano-structures. Previous researchers had utilized the surface energy concept to model the size dependent physical behavior of solids **[168-170].** It should be noted that the sign of the material length scales depends on elastic constants (derivatives of strain energy tensor) of the materials **[166, 167].** With the emerging technology of nanowire production, designing an actuating application based on these wires could advance nanotechnology to a new level. On the other hand, the mechanism of thermal actuation has been widely investigated and implemented to build MEMS actuators **[171]**. The ability to produce nanostructures by utilizing the already well developed micro fabrication technology is of advantage for the production process as well as for the integration of NEMS, MEMS, and ICs in constructing a fully functional device. The development of nanotechnology has brought the concept of mechanical actuation to a new stage in which synthesized nanoactuators are broadly applied in nanoelectromechanical systems such as nanometers, nanorobots, and nanosensors. Nanotube walls are promising for the use as movable elements in nanoelectromechanical systems owing to the arbitrary motion and controlled (with manipulators) relative motion executed by walls in multiwalled carbon nanotubes as well as to the extraordinary elastic properties exhibited by nanotubes .A number of devices that hold great promise for applications in nanoelectromechanical systems and are based on the use of the relative motion of the walls in carbon nanotubes have been proposed in recent years. Different nano- and microscale machines, devices and actuators have been devised and studied in **[172-174].** A Nanomachine and Nanoactuator Synthesis and Classification Solver is reported and demonstrated in **[174].** Nanoactuators performance depends upon nanomachine operating principle, topology, materials, etc. The piezoelectric model and the inertial drive model are developed **[175].** For accurate positioning, the resolution of the system is that of the actuator (scanning mode). The positioning rack system is realized at the Universities libre de Bruxelles **[176],** presents a machined steel rack with a rack step size of 300 mm and is actuated with Nitinol (shape memory alloy) wires. By using electro discharge wire cutting, the rack step could have a size of 20 mm **[177].** However, a rack system needs a lot of components that must be machined and assembled. Moreover, this positioning system does not allow backwards motion due to the asymmetry of the rack teeth. It is still to be chosen between the inertial drive principle and the crawling principle. Crawling could be miniaturized with success through a little more complex design **[178].** The inertial drive principle being chosen, an actuation principle is still needed. A few realizations have been proposed for the ten past years, with different forms and goals. Zesch **[175]** proposed a one-degree-of-freedom (DOF) impact drive NanoStep, actuated by two masses connected with a piezoelectric stack actuator and using a unique V-groove guiding rail. He also proposed a NanoCrab, which is a rotational micro motor based on the stick–slip principle, using three shear piezoelectric elements. At the ETHZ (Zurich, Switzerland), a stick– slip nano-

manipulator with the following characteristics has been realized by the Institute of Robotics: a resolution better than 10 nm and 4 DOF **[175].** They aimed at using it into a scanning electron microscope. Baumann **[179]** proposed a 3-DOF micro robot, based on stick–slip drive, that can position loads up to 1 g in a spherical workspace of 6 cm in diameter with a resolution of about 100 nm: Breguet and Clavel **[180]** developed a 1-DOF stick–slip actuator that reaches relatively high speeds (typically 5 mm=s) with a 1:5 mm range. Breguet and Renaud **[181]** proposed a very interesting 4-DOF micro robot using stick–slip piezoelectric actuators, that can rotate ðyzÞ and translate ðx; yÞ on a polished steel plate. A vertical axis ðzÞ is fixed on the platform and a V-groove supports four piezoelectric elements. At the University of Cambridge **[182],** the Deployable Structure Laboratory realized both linear and piezoelectric stick–slip actuators. Another point of interest is the lifetime of such an actuator: they can usually perform billions ð109Þ of cycles without loss of performance leading to a working time between 28 and 280 h with working frequencies between 10 and 1 kHz:. Inertial drive model the goal of this model **[175]** is to prove the stick–slip mechanism as a valid actuation principle.

2.4.1. Gaps in Research

1. There are hopes for applying nanorobots in medicine, but it may not be easy to do such a thing because of several drawbacks of such devices**.**
2. Graphene also has very complicated electric conductivity properties compared to traditional semiconductors as it lacks an energy band gap and essentially changes all the rules for how electrons move through a graphene based device.
3. The physical behavior of the torsional actuators has been extensively studied in micro scales not at nanoscales.
4. One of the most important effects that appear at nano-scale dimensions is the size dependency of material characteristics.
5. The mechanism of thermal actuation has been widely investigated and it under progress and needs more time to grow.
6. However, a rack system needs a lot of components that must be machined and assembled. Moreover, this positioning system does not allow backwards motion due to the asymmetry of the rack teeth.
7. It is still to be chosen between the inertial drive principle and the crawling principle. Crawling could be miniaturized with success through a little more complex design **[178].** The inertial drive principle being chosen, an actuation principle is still needed.
8. Crystalline silicon is still a complex and relatively expensive material to produce.
9. The key limitation of electron beam lithography is throughput, i.e., the very long time it takes to expose an entire silicon wafer or glass substrate. A long exposure time leaves the user vulnerable to beam drift or instability which may occur during the exposure. Also, the turn-around time for reworking or re-design is lengthened unnecessarily if the pattern is not being changed the second time.
10. Hydrofluoric acid is considered one of the more dangerous acids in the clean room. It penetrates the skin upon contact and it diffuses straight to the bone.
11. Integrated circuits are typically not combined with HAR silicon micromachining. The consensus of the industry at the moment seems to be that the flexibility and reduced process complexity obtained by having the two functions separated far outweighs the small penalty in packaging.
12. A forgotten history regarding surface micromachining revolved around the choice of polysilicon A or B.
13. Micro Production System is available in a lot of different levels of complexity.

14. Sorting mechanisms to orient these small micro-parts in a flowing process are not always useful, because the microparts stick at these alignment structures by adhesion.
15. But thermal expansions in the classical design of meter sized robots and actuators will already avoid a precise positioning.
16. When the size of a positioning system is doubled, a factor of 16 more acoustic noise will couple into it.
17. For assembly lines, the easy exchange of compatible positioners is necessary to reduce down time. Flexibility is also necessary, when new MEMS products are developed.
18. The combination of microassembly stages and microgrippers with classical CNC technology includes miscellaneous risks that may be new for both sides.
19. Some quality control instruments have to face an additional problem: an imprint to measure the hardness of a sample must be much smaller than the micropart that shall be analyzed.
20. Cantilevered nanotubes have also been shown as probes for the measurement of ultrasmall physical quantities, such as femto-gram mass , mass flow sensors , and pico-Newton order force sensors on the basis of their static deflections or change of resonant frequencies detected with an electron microscope. However, the deflections cannot be measured from micrographs in real-time, which limit the application of this kind of sensors.
21. Inter-electrode distance change caused emission current variation of a nanotube emitter may serve as a candidate to replace the microscope
22. The space of a TEM sample chamber is quite narrow and strictly limited due to the principle of a TEM, which includes a high vacuum environment, short distance between an upper and a lower polepiece, short working distance, and so on. These space limitations cause the difficulty of constructing multi-DOF manipulation systems inside a TEM sample chamber.
23. Despite all of the useful properties of carbon nanotubes and graphene for NEMS technology, both of these products face several hindrances to their implementation.
24. One of the main problems is carbon's response to real life environments.
25. Carbon nanotubes exhibit a large change in electronic properties when exposed to oxygen. Similarly, other changes to the electronic and mechanical attributes of carbon based materials must fully be explored before their implementation, especially because of their high surface area which can easily react with surrounding environments.
26. Graphene also has very complicated electric conductivity properties compared to traditional semiconductors as it lacks an energy band gap and essentially changes all the rules for how electrons move through a graphene based device .This means that traditional constructions of electronic devices will likely not work and completely new architectures must be designed for these new electronic devices.
27. The focus is currently shifting from experimental work towards practical applications and device structures that will implement and profit from the use of carbon nanotubes At this point in NEMS research, there is a general understanding of the properties of carbon nanotubes and graphene.
28. The next challenge to overcome involves understanding all of the properties of these carbon based tools, and using the properties to make efficient and durable NEMS with low failure rate- NEMS devices, if implemented into everyday technologies, could further reduce the size of modern devices and allow for better performing sensors.
29. At the same time no literature is available for selection of nanoactuator elements using multi attribute decision making (MADM) approach.
30. Relatively no one has contributed using combined approach of concurrent engineering design and design for x-abilities for designing nanodevices.

Work Done

Chapter-3

In this chapter, attribute knowledge base methodology for literature review based on different pertinent attributes of nanomaterial is proposed. The attribute based methodology highlights the attributes of the papers in particular areas in which various researchers have given their contribution.This methodology gives a quick review about the various papers in particular area of research. Methodology can be applied in smaller and bigger areas in the field of nanotechnology.

Chapter-4

In this chapter, an attempt is made to develop an integrated systems model for the structure of the nanotechnology system in terms of its constituents and interactions between the constituents and processes etc, using graph theory and matrix algebra. Different structural attributes of the nanotechnology system are identified to develop a graph theoretic model, a matrix model and a multinomial permanent model of the nanotechnology system. A top-down approach for complete analysis of any nanotechnology system is also given. A general methodology is also presented for characterization and comparison of two nanotechnology systems.

Chapter-5

This chapter deals with implementing a novel method to help the decision-maker for selection of a proper material that will meet all the requirements of the design engineers in this reliable and exhaustive data of nanomaterial is to generate and maintain based on their different pertinent attributes. It is useful for better understanding, comparison and analysis and for comparison; ranking and optimum selection of nanomaterial from a large number of nanomaterial available in global market, the multiple attribute decision making problems is solved by "TOPSIS" (Technique for Order Preferences by Similarity to Ideal Solution). The coding scheme and the selection procedures, mathematical and graphical, with example are also illustrated

Chapter-6

In this chapter to facilitate design of nanoactuator simultaneously for all x-abilities in an integrated way, a concurrent design methodology using multiple attribute decision making (MADM) approach is proposed. This concurrent design methodology is aimed at including design time considerably and makes use of expertises of experts from different specialized fields in a single design team. MADM approach provides technique for selection of best nanoactuator for the application under consideration. This design for x-abilities enables the designers to focus on various abilities at conceptual design stage on one hand and concurrent design approach helps reduce design time considerably.

CHAPTER-3

ATTRIBUTE KNOWLEDGEBASE METHODOLOGY

FOR

LITERATURE REVIEW

The present way of doing literature review has so many limitations. The area of nanotechnology and their uses are spread at very fast rate day by day. So it is very difficult to derive the appropriate knowledge in the area of nanomaterial. A lot of work has been done in the field of nanomaterial and lot of research is going on continuously to improve the various properties of nanomaterial. In this chapter, attribute knowledge base methodology for literature review based on different pertinent attributes of nanomaterial is proposed. The attribute based methodology is not only beneficial for academic research point of view but also for manufacturing firms producing various nanomaterial The attribute based methodology highlights the attributes of the papers in particular areas in which various researchers have given their contribution. According to the work done on different attributes, the academic value of the different papers and their coding can be done by using proposed methodology. With the same procedure an 'm x n' matrix is prepared having 'm' no of attributes and 'n' number of papers. This methodology does not only help a manufacturing firm who want to establish the business in that field, but also help to provide knowledge to researchers who want to work in the same area. This methodology gives a quick review about the various papers in particular area of research. Methodology can be applied in smaller and bigger areas in the field of nanotechnology. Here, demonstration is made on nanomaterial

3.1. Introduction

The focus of literature review is on different nanomaterial. The attributes discussed here are from their general aspect to different properties of the nanomaterial. Nanomaterial and nanotechnologies attract tremendous attention in recent research work. New physical properties and new technologies both in sample preparation and device fabrication evoke on account of the development of nanoscience. Nanotechnology is already an economic reality. The diversity and complexity of manufactured nanomaterial are continuously increasing: we are facing a fast growing, very heterogeneous class of materials which demand attention. Their unique characteristics that are in the first place related to their small sizes lead to important scientific and technological innovations in various sectors, but there are legitimate concerns that the same characteristics may cause new risks, that cannot always be assessed by the classical tools. Nanomaterial' means a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimension is in the size range 1 nm-100 nm. The occurrence of matter in nana dimensions comes with properties (chemical, mechanical, optical, etc.) often unexpected and completely different from those of the same materials at the micro- or macro-scale. In addition, nanomaterial comes in a wide variety of shapes: spherical particles, nanotubes, nanofibers, nanowires. Nanomaterial are now a major economic and technological opportunity for companies worldwide. Nanomaterial have an increasing impact in the new and emerging industries such as aerospace, computer, electronics and renewable energy, as well as in traditional industries such as food, cosmetics, automotive and construction. There are

numerous applications: drug delivery, anti-scratch paint, transparent sunscreens, more durable tires, anti-bacterial clothes, self-cleaning concrete, etc

3.2. Methodology

In this chapter, methodology is proposed which is very useful over the present way of doing literature review. This methodology is very useful with full of knowledge base. The methodology used in this is called Matrix methodology. In this methodology, an 'm x n' attribute information matrix is prepared. Various steps are involved in preparing this Matrix. From this Matrix, it is very easy to find out the academic value of any paper based on different attributes discussed in it. This can be applied in smaller and bigger areas of nanotechnology. Here, demonstration will be made by taking literature review of little nanomaterial. It is also to be extended in other directions of nanotechnology based upon the author recommendation.

Step- by Step procedure for Attribute based Literature review

Step-1 In this step, researchers/designers/manufacturers/users should decide their area, aims and objectives of literature review and gap analysis.

Step-2 In this step, cause and effect diagram is prepared to identify all the groups/subgroups of attributes required to be studied.

Step-3 In this step, prepare a list of all the attributes identified by cause and effect diagram or from different research publications selected for literature review.

Step-4 In this step, characterization of papers can be done with respect to 'm' number of attributes as

$$Pj = \left[A_{1j}, A_{2j}, A_{3j}, \ldots\ldots\ldots\ldots\ldots\ A_{ij}, A_{mj} \right] \text{, where, } i = 1, 2, 3, m$$

Step-5 In this step, define 'm x n' knowledge base Matrix (or 'm x n' information Matrix), where rows represents attributes and columns represent research papers.

Step-6 In this step, every attribute is coded in the interval scale of 0-5 based on depth of study has been done in a particular paper. (i.e. code 5 represents the attribute very high studied, code 4 represents highly studied, code 3 represents average studied, code 2 represents less studied, code 1 represents very less studied and code 0 for absent (i.e. that particular attribute is totally absent in papers).

Step-7 In this step, prepare a comprehensive knowledge base Matrix for all the 'n' papers collected from all sources related to area under consideration. It is preferably to develop user friendly software for permanent storage and retrieval and for upgrading purpose.

Step-8 In this step, summation of weights of all the attributes in the i^{th} row (represents the interest and depth of study of different attributes) is calculated. Similarly, summation of weights of all the papers in the j^{th} column (represents the academic importance of different papers with respect to particular attributes) is calculated.

3.2.1. Identification of Research papers

The first step in developing the attribute information matrix is to identify the various research papers and research publications related to different nanomaterial. The research papers are

characterized during different periods of time. The research papers and publications are identified through various internet links and through colleges and research institutes related to different nanomaterial etc.

3.2.2. Grouping of research papers

In this, identified research papers/publications are grouped according to their year of publication. The grouping of different papers can be done in four different ways. Firstly, grouping of research papers and publications according to different periods of time, like from 1995-2000, (2001-2005), (2006-2010) and (2010-2015) and onwards.

Secondly, grouping of research papers and publications according to their scientific index/impact factor. Thirdly, grouping of research papers and publications according to subject /area wise. Fourthly, grouping of research papers and publications according to different categories as review papers, article papers, conferences and patents etc. The grouping of papers is necessary to understand what has been done and what has not been done during that period of time. what are the different procedures, tools, techniques, methods that many researchers opt, different issues on which more discussion and work is carry out till today are easily identified. The step provides the knowledge about the various developments in the field of nanomaterial.

3.2.3. Coding of research papers

In this, coding of different research papers identified is done. The coding of the research papers can be done in the interval scale of 0-5. Coding can be done on the basis of highly studied, average studied, very less studied and absent, attributes with respect to the corresponding papers.

While coding, several factors are kept in mind, like, depth of analysis on particular attribute, scientific index/impact factor of journal, Level of publishing journal etc. The coding scheme for research papers as shown in **Table-1.14.**

Categories	Codes
Attribute which is very high studied with respect to its corresponding paper	5
Attribute which is highly studied with respect to its corresponding paper	4
Attribute which is average studied with respect to its corresponding paper	3
Attribute which is less studied with respect to its corresponding paper	2
Attribute which is very less studied with respect to its corresponding paper	1
Attribute which is absent	0

Table-1.14. coding scheme for research papers

3.3. Cause and effect analysis for attributes identifications

Cause and effect analysis is used for identification of different attributes and their effect to decide the academic value of different attributes. In this paper, various causes and their effect are found out which are important to produce a good quality nanomaterial products in terms of academic value of papers.

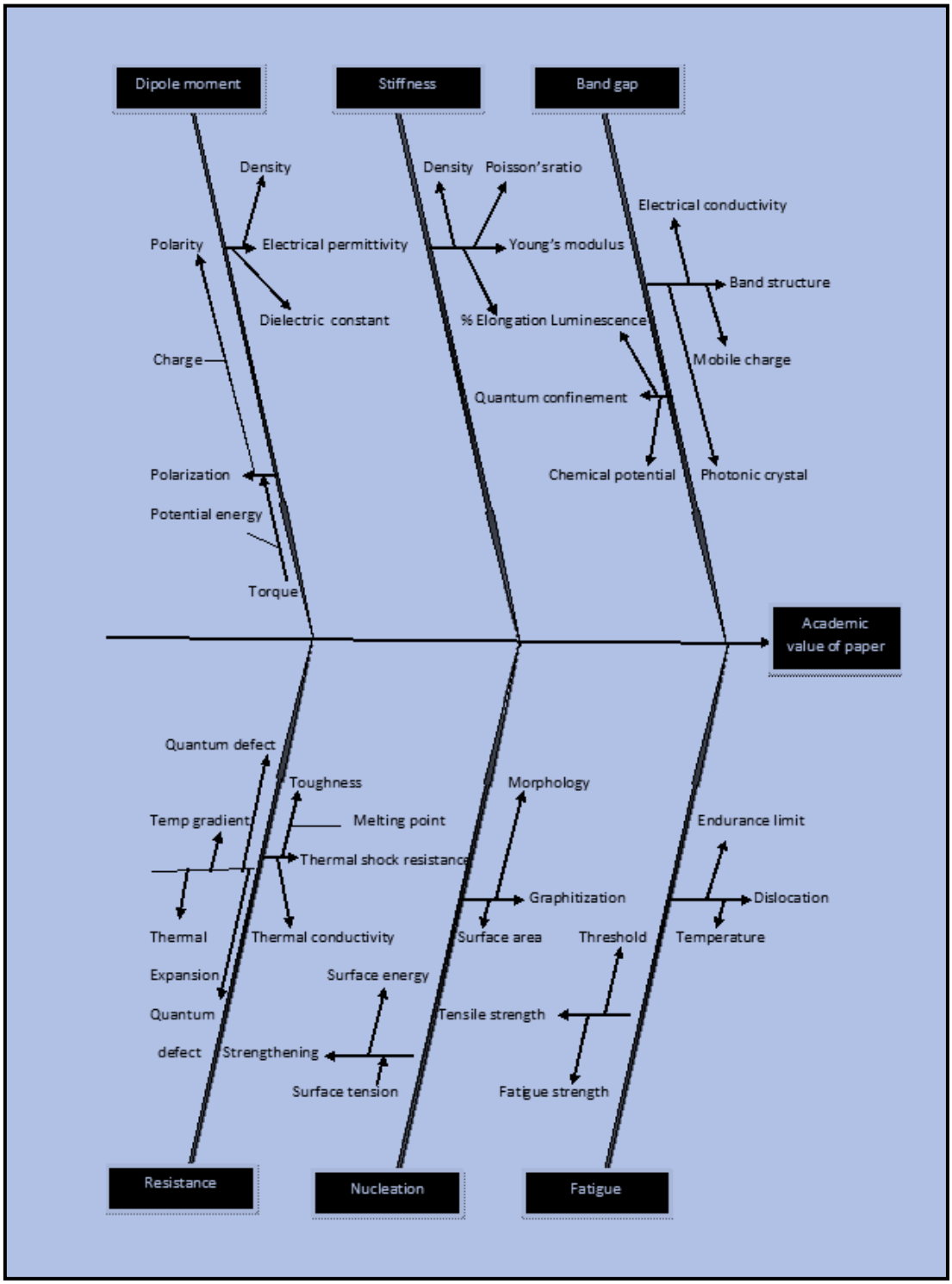


Figure-1.92.Cause and effect analysis of research publications/academic value of papers

Cause and effect analysis is one of the tools which are used to produce good quality product from past many years. Using cause and effect diagram, all the groups and subgroups of attributes are identified as shown in **Figure-1.92.**

3.3.1. Identification of Attributes

The second step in developing the attribute information matrix is to identify all the relevant attributes from different research publications. The attributes identified are those having significant effect on the various characteristics of nanomaterial.

The attributes are identified from the manufacturing to the application of nanomaterial in the various field e.g. transition temperature, fragility, morphology etc has an effect on polymers with an increase in fullerene content and temperature,

Table-1.15. shows the various attributes which are identified from different research papers have significant effect on nanomaterial properties. Here, 168 attributes are identified from 68 papers which are related to different properties and mechanical behaviours of nanomaterial and affect the various characteristics in different ways as shown in **Table-1.15**.

General Attributes	
1. Malleability	2. Polymorphism
3. Ductility	4. Surface topology
5. Lustrous	6. Structural bond forces
7. Softness	8. Ionic distribution
9. Durability	10. Dielectric relaxation
11. Molecular weight	12. Stiffness
13. Resistance to oxidation	14. Capacitance stability
15. Resistance to corrosion	16. Granularity
17. Conductivity of electricity	18. Dimensional stability
19. Surface Plasmon resonance	20. Transparency
21. Chemical reactivity	22. Power loss factor
23. Colour	24. Point adhesion
25. Internal reflection	26. Magnetic ordering
27. Phase	28. Resistance to deformation
29. Capable of transmitting light	30. Specific surface area
31. Index of refraction	32. Crystallite size

33. Lubricate	34. Crystal phase
35. Strength	36. Reaction rate
37. Resistance to neutron radiation	38. Catalytic selectivity
39. Rigidity	40. Debye wall factor
41. Wear resistance	42. BENS broadening
43. Biocompatibility	44. Fragility
45. Film friction coefficient	46. Current density
47. Impact sensitive	48. Resistance to arcing
49. Toughness	50. Orbit hybridization
51. Dispersion	52. Metallic behaviour
53. Reinforcement	54. Aspect ratio
55. Stability	56. Radial elasticity
57. Solubility	58. Symmetry
59. Brittleness	60. Polari ability
61. Resistance to high temperature	62. Taper ratio
63. Strengthening	64. Light weight
65. Substrate	66. Ballistic resistance capacity
67. Relative chemical inertia	68. Toxicity
69. Robustness	70. Angle of incidence
71. Monoclinic	72. Electromagnetic resonance
73. Dielectric breakdown	74. Crystal structure
75. Resistance to cracking	76. Thermo ionic
	77 Work function
Physical Attributes	
78.Density	79. Platy
80.True density	81. Specific suspension
82.Melting point	83. Resilience
84.Boling point	85. Bulk density

86.Heat of fusion	87. Decomposition temperature
88.Heat of vaporization	89. Threshold electric field
90. Molar heat capacity	91. Binding energies
92. Lattice constant	93. Catalyst
94. Metallic radius	95. Curvature energies
96. Gas solid liquid	97. String tension
98. Wavelength	99. Diameter
100. Morphology	101. Particle size
102. Bond distance	103. Emissivity
104. Purity	105. Richard constant
106. Molar density	107. Hardness
108. Dielectric	109. Length
110. Hydrophilic	111. Brightness
	112. Short term beam stability
Mechanical Attributes	
113.Tensile strength	114. Compression yield strength
115. Young's modulus	116. Coefficient of friction
117. Shear modulus	118. Flexural strength
119. Bulk modulus	120. Percentage elongation
121. Poisson's ratio	122. Impact strength
123. Mohr hardness	124. Deformation stress
125. Vickers hardness	126. Van der wall forces
127. Brinell hardness	128. Internal surface area
129. Knoop hardness	130. Specific strength
	131. Fracture toughness
Atomic Attributes	
132.Oxidation states	133.Atomic radius
134.Electro-negativity	135.Covalent radius

136 Ionization energies	137.Van der wall radius
Electrical Attributes	
138. Electrical resistivity	139. Electrical performance
140. Dielectric constant	141. Superconductivity
142. Dielectric strength	143. Conductance quantization
144. Band structure	145. Band gap
146. Curvature effects	147. Electrical conductivity

Thermal Attributes	
148. Thermal conductivity	149. Thermal stability
150. Thermal expansion	151. Thermal source
152. Specific heat	153. Coefficient of thermal expansion
154. Temperature	155. Ballistic conductance
156. Standard entropy	157. Temperature stability
158. Standard enthalpy of formation	159. Phonon mean free path
160. Nucleation	161. Relaxation time
Optical Attributes	
162. Transmission	163. Absorption
164. Luminescence	165. Photo-luminescence
166. Index of refraction	167. Surface Plasmon
	168. Oscillation

Table-1.15. List of attributes identified from different research publications

From all these attributes any researcher can easily predict on which papers and on which attribute, more concentration is given by different researchers and in what depth work has been done on particular attribute.

3.3.2. Coding of attributes

Ranking or coding of identified attributes can be done on the basis, highly studied, less studied and attributes which is very useful in the interval scale from 0-5 by team of experts of respective area selected for research as shown in **Table-1.16.**

Categories	Codes
Absent	0
Very less studied attributes	1
Less studied attributes	2
Average Studied attributes	3
Highly studied attributes	4
Very highly studied attributes	5

Table-1.16. Coding scheme for attributes

Which defines 0 for absent, 1 for very less studied, 2 for less studied, 3 for average studied, 4 for highly studied and 5 for very high studied and on basis of this one can easily found out on which attribute more study has been done and to how much depth.

3.4. Procedure to develop a Attribute Information Matrix

1. In the attribute information Matrix, all the rows represent the number of attributes which are related to the nanomaterial and have significant effect on the various physical and mechanical properties.

   The attributes/ research issues/property are represented by 'A_i', where 'i' varies from 1 to 'm' and 'm' represents the m^{th} attribute and the column represents the number of papers. The papers are represented by 'P_j', where 'j' varies from 1 to 'n' .Where 'n' represents the n^{th} paper. Then there is formation of 'm x n' Matrix.

2. First column of the Matrix represents the first paper.

3. First row represents the first attribute find out from the research publications.

4. In this attribute information Matrix 'A_{ij}' represents the inheritance/ presence/depth of analysis modelling etc, of the ith attribute in the jth paper on the interval scale of 0-5.

5. ΣA_i denotes the submission total of all the values of attributes along each row with respect to the corresponding papers.

6. ΣP_n denotes the submission total of all the values of different papers along column wise with respect to the corresponding attributes.

7. Lastly, Σ_{total} represents the total sum corresponding to both attributes and papers.

From, ΣA_i and ΣP_n the academic value of each paper is decided. Attribute Information Matrix. shown in **Table-1.17**.

		Papers										
		P1	P2	.	.	.	Pj	.	.	.	Pn	ΣAi
	A1	.	.	.	.	.	.	.	.	.	.	ΣA_1
	A2	.	.	.	.	.	.	.	.	.	.	ΣA_2
	.	.	.	.	.	.	.	.	.	.	.	.
	.	.	.	.	.	.	.	.	.	.	.	.
	.	.	.	.	.	.	.	.	.	.	.	.
	.	.	.	.	.	.	.	.	.	.	.	.
Attributes	Ai.	.	.	.	.	.	Aij	.	.	.	.	ΣA_i
	.	.	.	.	.	.	.	.	.	.	.	.
	.	.	.	.	.	.	.	.	.	.	.	.
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	.	.	.	.	.	.	.	.	.	.	.	.
	Am	.	.	.	.	.	.	.	.	.	.	ΣA_m
	ΣPn	ΣP_1	ΣP_2	.	.	.	ΣP_j	.	.	.	ΣP_n	Σ_{total}

Table-1.17. Attribute information matrix 'm x n'

From the Attribute Information Matrix, the academic value of corresponding papers with respect to the particular attribute is found out. The summation of the attributes and papers can be calculated as follows:-

For Attributes:-

$$\Sigma A_i = \Sigma A_1 + \Sigma A_2 + \Sigma A_3 + \cdots\cdots\cdots\cdots + \Sigma A_m \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Where, ΣA_i represents sum of 'm' attributes

For Papers:-

$$\Sigma P_n = \Sigma P_1 + \Sigma P_2 + \Sigma P_3 + \cdots\cdots\cdots\cdots + \Sigma P_n \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Where, ΣP_n represents sum of 'n' papers.

The value of 'A_{ij}' of i^{th} attribute with respect to j^{th} paper can be given as:-

$$\Sigma A_{ij} = \Sigma A_i + \Sigma P_j \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

3.5. Advantages of the Attribute Information Matrix

The Attribute Information Matrix above formed having a large number of advantages. Attribute Information Matrix is used as a full source of deriving information and knowledge

from different research publications/papers for researcher/designer/manufacturer etc for their basic and commercial research purposes. The proposed methodology is also useful with respect to time, cost, efforts, knowledge, storage and retrieval and also for the up gradation etc.

3.6. Usefulness of the Proposed methodology

I. The Attribute Information Matrix is useful for researchers as a source of knowledge and information. This Matrix provides the appropriate knowledge about all the attributes discussed in a particular paper.

II. The Attribute Information Matrix is also useful for designers and manufacturers to derive the knowledge for the commercial research and for the development of new nanodevices and nanoproducts.

III. The Attribute Information Matrix is also useful from time point of view because it saves lots of time in analyzing the large number of different research publications/papers in short span of time.

IV. The Attribute Information Matrix also reduces lots of efforts and cost involved to derive out the information from the research publications/papers.

V. The Attribute Information Matrix behave as a database/software which can be used for storage and retrieval of the information from research publications which is to be updated and extended as per the requirements/changing needs/trends of research etc.

VI. Library, where this software is installed is to be maintain and upgrade for giving full benefits to all the customers/stakeholders/researchers etc.

3.7. Gap analysis

The next step in proposed methodology is to do gap analysis to find out gap from the past work. With the help of Attribute Information Matrix, it is very easy to find out the gap from the literature available over the periods of time. By this way, it is easy to decide in which direction anyone can put his contribution towards their goal. Gap analysis is different for different people in accordance with their area what they have chosen.

3.7.1. Importance of gap analysis

I. **Researcher:-**From the Attribute Information Matrix, it is easy for a researcher to find out the gap between their works, i.e. what has been done or what has not been done. As students of PhD have to spend much of their time on literature review during course to find out the gap in the research from where they can proceed further. Using this methodology, software can be uploaded in the library of colleges which is to be updated as per the new requirement of researchers. Even, M.E students can also used this software for their thesis work in selecting the most appropriate area of research according to their interest.

II. **Designer:-** As we know that, every industry has their own research and development department where a designer continuously try to update the product quality by modifying the designs of the new or existing products with the changing in the demands of the customer/user etc. For this, designer can go through different types of researches with the product in order to develop a new design which helps in increasing the productivity and

profit of the industry with least input cost. By using this type of Attribute Information Matrix, it is very easy for any designer to find out the various aspects which helps him to make their design better and productive.

III. **Manufacturer:-**When any manufacturer has to produce a new product there are various aspects which needs to be consider those effects the different properties in different ways. But there are few aspects, which are most required in the product. With the use of Attribute Information Matrix, it is very easy to evaluate the various manufacturing aspects those give the desired properties, what are the manufacturing parameters that can make the product quality and cost effective. For the person, who want to establish a new industry for them this Attribute Information Matrix provides all the related manufacturing aspects which boost them in establishing the industry.

IV. **Short term and long term strategic point:-**Attribute Information matrix is very important for any firm to make their good strategy. By Attribute Information Matrix, they can easily know about the various trends of research changes from past years to today scenario. Accordingly by keeping these points in mind a good strategy plan can be made in accordance with their field of work.

3.8. Illustrative example of Attribute Information Matrix

Following table5 show the example of Attribute Information Matrix, i.e. how this matrix is used. In this Matrix, 20 attributes are selected with respect to the corresponding 20 papers.

		Publications/Papers																				
		P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	P13	P14	P15	P16	P1	P18	P19	P20	
	References of Papers	[54]	[6]	[34]	[44]	[23]	[39]	[30]	[36]	[38]	[51]	[56]	[13]	[60]	[1]	[5]	[9]	[19]	[29]	[43]	[45]	
S/No	Attributes																					∑Ai
	Ai, i=1,.....m																					
A1	Young's modulus	2	0	4	0	1	0	0	1	5	0	0	5	0	0	0	0	0	0	0	1	19
A2	Tensile loading	5	0	0	0	0	0	4	0	0	1	0	2	0	4	3	1	2	0	0	0	22
A3	Diameter	0	1	3	2	0	1	0	0	0	0	5	0	1	0	0	0	0	3	5	0	21
A4	Temperature	0	0	0	5	2	5	0	4	2	5	0	0	0	2	0	0	0	0	0	5	30
A5	Morphology	1	0	0	0	2	5	1	0	0	0	0	4	5	2	4	2	5	0	0	0	31
A6	Resistance	0	0	0	0	5	0	0	0	0	5	5	0	0	0	0	0	0	2	0	0	17
A7	Mechanical behaviour	0	5	0	4	0	0	0	2	5	2	0	0	0	0	2	0	0	0	4	3	27
A8	Load transfer	0	0	2	0	0	0	0	0	2	0	0	0	0	5	0	0	0	1	0	0	10
A9	Fracture toughness	3	0	0	0	0	3	2	0	0	5	0	5	0	0	0	0	3	0	0	0	21
A10	Solubility	0	0	0	3	5	0	0	0	0	0	4	0	4	5	0	3	0	0	0	0	24
A11	Dispersion	0	4	0	0	0	0	0	0	0	0	0	0	0	5	0	0	0	5	3	0	17
A12	Thermal conductivity	0	0	5	0	0	0	0	2	0	3	0	0	0	0	0	0	0	0	0	4	14
A13	Toxicity	0	0	0	0	4	2	0	0	3	0	1	0	0	0	5	0	0	0	0	0	15
A14	Band gap	0	3	0	0	0	0	3	0	0	0	0	0	0	0	0	0	0	0	2	0	8
A15	Compressive response	5	0	0	0	0	0	0	5	0	0	2	3	5	3	0	4	4	0	0	0	31
A16	Electric field	0	0	3	2	0	0	0	0	0	4	0	0	0	0	0	0	0	0	0	0	9
A17	Electrical transport	0	0	0	0	5	0	0	0	1	0	0	0	2	0	4	0	0	4	1	0	17
A18	Mechanical strngth	0	2	0	0	0	0	5	0	0	0	3	2	0	2	0	5	1	0	0	5	25
A19	Hardness	0	0	4	1	0	4	0	0	4	5	0	5	0	1	0	0	0	1	0	0	25
A20	Graphitization	4	0	1	0	0	0	0	3	0	5	0	0	0	0	1	0	3	0	5	0	22
	∑Pn	20	15	22	17	24	20	15	17	22	35	20	26	17	29	19	15	18	16	20	18	Total

Table-1.18.Attribute information matrix for 20 papers and 20 attributes

After selecting, papers and attributes coding of different attributes with respect to their corresponding papers can be done by using table 2 and procedure to develop a Attribute Information Matrix is followed, where $\sum A_i$ and $\sum P_n$ for all the attributes with respect to their corresponding paper is calculated as shown in **Table-1.18**.

3.9. SWOT Analysis

SWOT analysis is a strategic planning method, which is used to evaluate the strength, weakness, opportunities and threats in a project, research or in a business venture.

Strength: - It is the characteristics of a project team that gives advantages over others.

Weakness:-It is a characteristic that put the team in loss/disadvantage relative to others.

Opportunities:-These are the external chances to improve the performance.

Threats:-External elements in the environment that cause the trouble for the project.

In this paper, SWOT analysis is done in accordance to manufacturer, designer and researcher point of view as shown in **Figure-1.93, Figure-1.94 and Figure-1.95**.

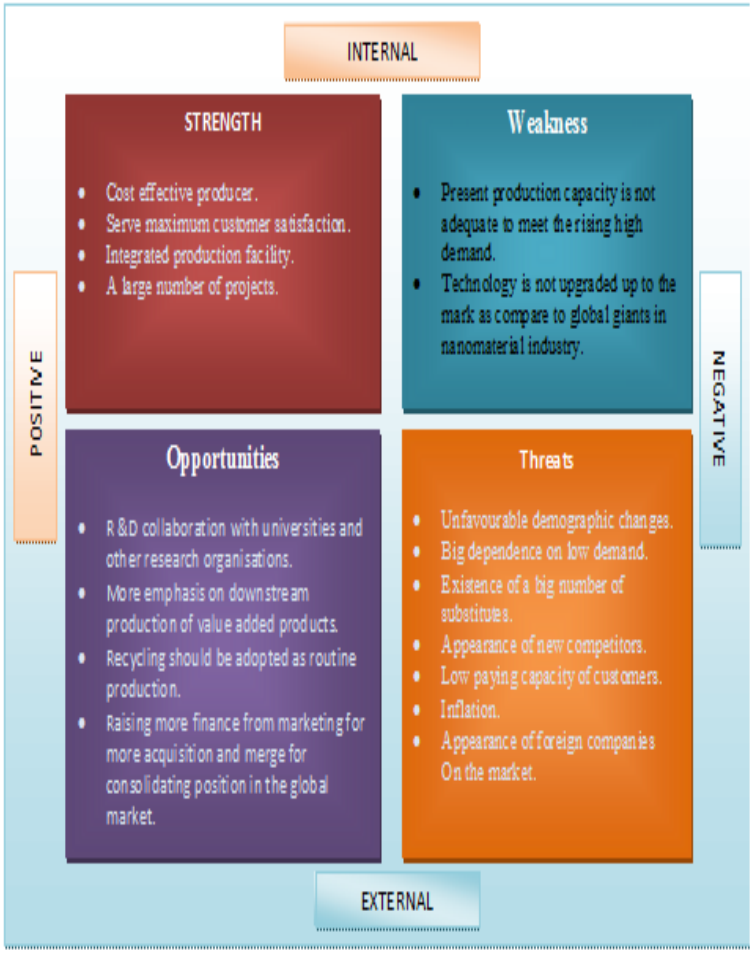

Figure-1.93.SWOT analyses for manufacturer

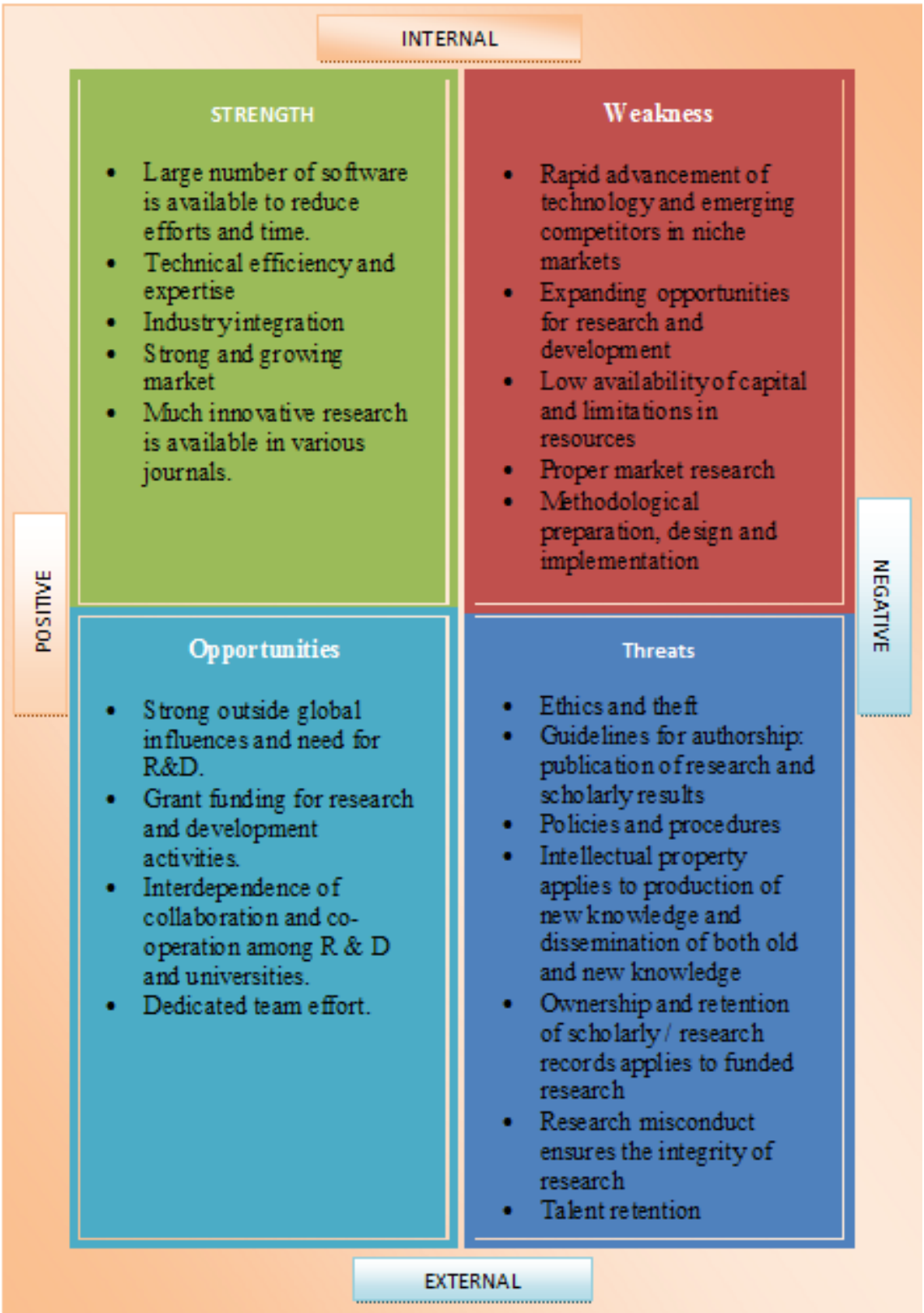

Figure-1.94.SWOT analyses for designer

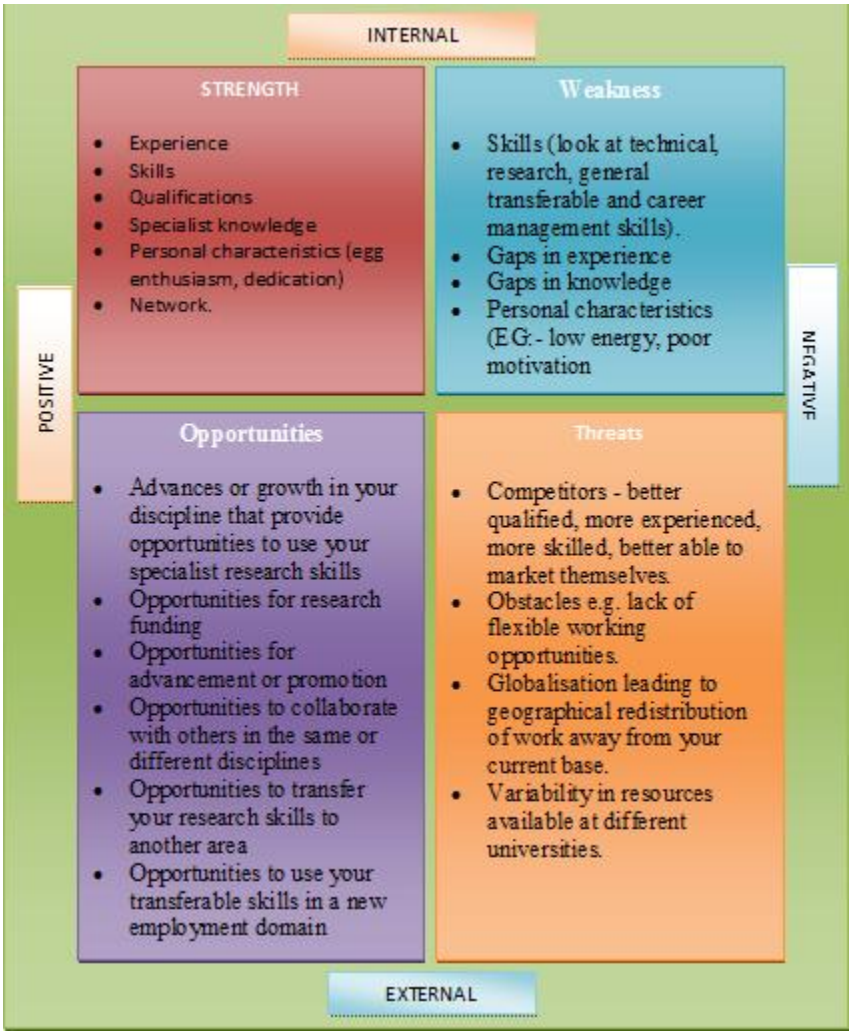

Figure-1.95.SWOT analyses for researcher

Important Notes

- Through interactions with the software of knowledge base Matrix, anyone can easily identify any numbers of papers of his choice of particular attributes from Matrix.
- Knowledge base Matrix clearly highlights, which attribute has not been studied and which has been studied or in what depth it is studied.
- It is recommended that researcher/designer/manufacturer should carry out SWOT analysis before deciding any short term or long term strategy.
- It is necessary to update the knowledge base Matrix time to time as per the requirements of the different researchers/designers..... etc. So that changes in the trends of the research are easily monitored. The owner of this Matrix software, having a great responsibility to update this Matrix software everyday to make this as a good source of information based knowledge as a library.

3.10. Concluding Remarks

Here, represents attribute based literature review methodology with knowledge base. In which different attributes are identified on the basis of cause and effect diagram. Proper identification of different attributes and their quantification, coding has been done in a very efficient and reliable manner. Methodology helps the different researchers, designer, manufacturer and industrialist by providing them those attributes which are benefited for their respective field of work. Identification of different research papers and sorting of those papers based on application, process, techniques etc in which more or less work is done are easily calculated. Methodology provide a computer based information Matrix software with the help of which relative importance of any attributes with respect to any paper can be easily determined. Different issues are addressed in a very effective manner with the help of information Matrix. Information Matrix is a permanent source of knowledge and need to be updated so that everyone takes more benefit from database. Here methodology is proposed only for nanomaterial, but it can also extended by the recommendation of the author in all the areas of nanotechnology.

CHAPTER-4

STRUCTURAL MODELLING, CHARACTERIZATION AND INTEGRATIVE ANALYSIS OF NANOTECHNOLOGY SYSTEM

"Graph Theory Approach"

In this chapter, an attempt is made to develop an integrated systems model for the structure of the nanotechnology system in terms of its constituents and interactions between the constituents and processes etc, using graph theory and matrix algebra. The nanotechnology system is first modelled with the help of graph theory, then by a variable adjacency matrix and then by a multinomial known as a permanent function. The permanent function provides an opportunity to carry out structural analysis of the nanotechnology system in terms of strength, weakness, improvement and optimization by correlating the different system with its structure. A physical meaning has been associated with each term of the permanent function. Different structural attributes of the nanotechnology system are identified to develop a graph theoretic model, a matrix model and a multinomial permanent model of the nanotechnology system. A top-down approach for complete analysis of any nanotechnology system is also given. A general methodology is also presented for characterization and comparison of two nanotechnology systems. Usefulness of the present methodology is also illustrated

4.1. Introduction

Nanotechnology (sometimes shortened to "nanotech") is the study of manipulating matter on an atomic and molecular scale. Generally, nanotechnology deals with developing materials, devices, or other structures possessing at least one dimension sized from 1 to 100 nanometres. A material such as gold, which is chemically inert at normal scales, can serve as a potent chemical catalyst at nanoscales. Much of the fascination with nanotechnology stems from these quantum and surface phenomena that matter exhibits at the nanoscale. Two main approaches are used in nanotechnology. In the "bottom-up" approach, materials and devices are built from molecular components which assemble themselves chemically by principles of molecular recognition. In the "top-down" approach, nano-objects are constructed from larger entities without atomic-level control. Nanotechnology is considered a key technology for the future. Nanotechnology entails the application of fields of science as diverse as surface science, organic chemistry, molecular biology, semiconductor physics, micro-fabrication, etc. Nanotechnology distinct from devices which are merely miniaturized versions of an equivalent macroscopic device; such devices are on a larger scale and come under the description of microtechnology. Another group of nanotechnological techniques include those used for fabrication of nanotubes and nanowires, those used in semiconductor fabrication such as deep ultraviolet lithography, electron beam lithography etc techniques such as those employing di-block copolymers..Most applications are limited to the use of

"first generation" passive nanomaterials which includes titanium dioxide in sunscreen, cosmetics, surface coatings and some food products; Carbon allotropes used to produce gecko tape; silver in food packaging, clothing, disinfectants and household appliances; zinc oxide in sunscreens and cosmetics, surface coatings, paints and outdoor furniture varnishes; and cerium oxide as a fuel catalyst. We proposed a new integrated systems approach that can help in getting good competing benefits, high overall performance and good quality of product in a shorter time. The present work is derived from various research areas like quantitative structure activity relationship (QSAR) and quantitative structure properties relationship (QSPR) **[196],** virtual design, and virtual prototyping **[197].**

4.2. Assumptions for developing graph theoretic model

The proposed graph theoretic model for nanotechnology systems is based on some assumptions as listed below:-

- The structure of the system can be correlated quantitatively with its performance, e.g. productivity, quality, reliability.
- The interactions as well as the subsystems discussed are assumed for a general nanotechnology system. The subsystems must be identified separately for applying the model to any specific nanotechnology system.
- Nanotechnology system, its subsystems and their interactions for the organization under consideration depends upon its aims and objectives, value system etc.
- Variable permanent matrix is capable of storing complete information related to a real life situation of a typical nanotechnology system as all its elements are variables and fuctions of characterizing attributes representing subsystems (i.e. diagonal elements) and interconnections (i.e. off diagonal elements). These attributes if identified comprehensively, the matrix represents the nanotechnology system completely.
- Permanent function of the variable permanent matrix characterizes uniquely the nanotechnology system form the point view of the structure.
- Performance of a nanotechnology system depends on individual performance of subsystems, sub-systems and their components along with interactions/interdependences/ influences between them.
- Modelling/methodology are based on bottom-up approach. Permanent function values of sub-subsystems are used in permanent matrices of subsystems. Permanent function values of subsystems are used to calculate permanent functions of nanotechnology system.
- The experts may assign correct and representative score to the elements of the manufacturing system at the lowest level in a particular dimension of performance.

4.3. Modelling of Nanotechnology System

4.3.1. Identification of subsystems of the nanotechnology system

For description of the methodology, five subsystems have been identified namely, nanomaterial, nanofabrication, nanostructure, nanomachining, nanomanipulation subsystems. This is a representative assumption for a general nanotechnology system and the entire important criterion governing the nanotechnology behaviour reflected in these subsystems. These subsystems may not be universal and there may be some variations for modelling, specific nanotechnology system. However the proposed model has a capability to consider

any such variations and is suitable for modelling any particular nanotechnology system structure. The following sections discuss the importance of each of the identified subsystems of the nanotechnology system.

4.3.1.1. Nanomaterial subsystem

Various types of nanomaterial subsystem for a general nanotechnology system may be listed as attributes, properties, reactivity, nucleation, characteristics, compositions, agglomeration, structure etc. An important aspect of nanotechnology is the vastly increased ratio of surface area to volume present in many nanoscale materials, which makes possible new quantum mechanical effects. Nanomaterial is a field that takes a materials science-based approach to nanotechnology. Nanomaterial generally falls into two categories: fullerenes, and inorganic nanoparticles. It studies materials with morphological features on the nanoscale, and especially those that have special properties stemming from their nanoscale dimensions Also the uncontrolled agglomeration of powders due to attractive van der Waals forces can also give rise to in micro structural in homogeneities. There are different methods having different techniques for characterizing particle size distribution. This characterization is imperative because many materials that are expected to be nano-sized are actually aggregated in solutions. Some of methods are based on light scattering. Other apply ultrasound, such as ultrasound attenuation spectroscopy for testing concentrated nano-dispersions and micro emulsions etc. All the subsystems of nanomaterial can integrate in such a way that every aspect of each subsystem is important to improve the characteristic features of new nanomaterial.

4.3.1.2. Nanofabrication subsystem

Nanofabrication subsystem is mainly concerned with nanolithography, which is a branch of nanotechnology concerned with the study and application of fabricating nanometre-scale structures, meaning patterns with at least one lateral dimension between the size of an individual atom and approximately 100 nm. Nanolithography is used during the fabrication of leading-edge semiconductor integrated circuits (nanocircuitry) or nano-electromechanical systems (NEMS).As of 2007, nanolithography is a very active area of research in academia and in industry. Scanning probe lithography (SPL) is a promising tool for patterning at the deep nanometre-scale. For example, individual atoms may be manipulated using the tip of a scanning tunnelling microscope (STM). Dip-Pen Nanolithography (DPN) is the first commercially available SPL technology based on atomic force microscopy. Where atomic force microscopic nanolithography (AFM) is a chemo mechanical surface patterning technique that uses an atomic force microscope**.[183]** Nanosphere lithography uses self-assembled monolayer's of spheres (typically made of polystyrene) as evaporation masks. This method has been used to fabricate arrays of gold nanodots with precisely controlled spacing's **[184].** All subsystems of nanofabrication can lead to techniques that are used to produce nanoscale devices and benefited the consumer with applications that are benefited in their future scope.

4.3.1.3. Nanostructure subsystem

A nanostructure is an object of intermediate size between molecular and microscopic (micrometer-sized) structures. In describing nanostructures it is necessary to differentiate between the numbers of dimensions on the nanoscale. Nanotextured surfaces have one dimension on the nanoscale. Scanning electron microscopes have been used by researchers

since 1935 to examine micrometer scale structures and more often recently to examine nanoscale structures. This is a versatile technique with which relatively large samples can be visualized, dimensional measurements can be taken and comparison analysis can be performed. For topology and geometries of nanostructures the imaging modes allow the mapping of surface properties. These include atomic force microscopy, pulsed force microscopy, scanning tunnelling microscopy etc which maps the mechanical properties. Nanostructures are unique as compared with both individual atoms/molecules at a smaller scale and the macroscopic bulk materials. They are also called mesoscopic structures. Measurement and integration techniques play very important role in measuring the dimensions and to integrate them. Nanoscience research focuses on the unique properties of nanoscale structures and materials that do not exist (or only very weakly exist) in structures of same material composition but at other scale ranges.

4.3.1.4. Nanomachining subsystem

The scientific study will result in the formation of the theoretical basis of nanometric machining, which enables the better understanding of nanometric physics and the development of its controllable techniques to meet the advanced requirements of nanotechnology and nanoscience**.** More specifically, nanorobotics refers to the nanotechnology engineering discipline of designing and building nanorobots, with devices ranging in size from 0.1-10 micrometers and constructed of nanoscale or molecular components **[185, 186]** The names nanobots, nanoids, nanites, nanomachines or nanomites have also been used to describe these devices currently under research and development **[187,188]**. Nanomachines are largely in the research-and-development phase **[189]** but some primitive molecular machines have been tested. An example is a sensor having a switch approximately 1.5 nanometres across, capable of counting specific molecules in a chemical sample. The first useful applications of nanomachines might be in medical technology**[190]** which could be used to identify and destroy cancer cells **[191, 192]** Deterministic mechanical, loose abrasive, mechanical and non- mechanical nanometric machining is indispensable to manufacturing complex micro and miniature structures, components and products in a variety of engineering materials. Nanometric machining can be applied in bulk machining of silicon, aluminium substrates for computer memory, disks etc. It is also very promising in the production of sensors, accelerometer, actuators, micro-mirror, etc. The indispensable advantage of nanometric machining is its applicability to manufacture 3D complex components/devices including micro moulds, dies and embossing tooling for cheap mass production of optical parts etc. Therefore, it is undoubtedly one to the major enabling technologies for commercialization of nanotechnology in the future.

4.3.1.5. Nanomanipulation subsystem

Nanomanipulation is a technology to manipulate a small object sized in nanometre to submicron scale. Optical tweezers is one of nanomanipulation techniques, which can investigate pico-newton to femto-newton force exerted on microscopic objects. Nanomanipulation of nanoparticles has been widespread of interest for the last years, and dynamic modelling is a basic tool for understanding the pushing procedure at real time. The initial model for pushing was provided by Falvo **[193],** but in this model, the forces due to the scale changing were not considered. The first model that considers surface forces and contact deformations is proposed by Sitti **[194].** It uses Johnson–Kendall–Roberts (JKR) theory of contact mechanics in which a discrete system model is used to design tele-operating control of pushing. The experiment done in this is very close to what Guangyong Li and Ning Xi

have done. Both works indicate nanoparticle nanomanipulation in a virtual reality environment **[195].** Virtual Reality method is one of the newest methods which create a virtual and multimedia environment similar to actual environment so that the user can feel the sense of being placed in the actual environment by just watching it. Nanomanipulator has been built to perform nanomanipulation studies under vacuum inside a scanning electron microscope. Two researches at Harvard University have created a nanoscale grasping device ideal for measuring and manipulating molecular structures. Nanorobots are nanodevices that will be used for the purpose of maintaining and protecting the human body against pathogens. Single atom manipulation can be achieved with appropriate selection of the charge, the magnitude, and duration of voltage pulse applied between the STM tip and the sample surface.

4.4. Characterization of Nanotechnology System

"Graph theoretic representation

A nanotechnology is considered to be a collection of a number of basic constituents, e.g., manipulation and fabrication as shown in **Figure-1.96**.

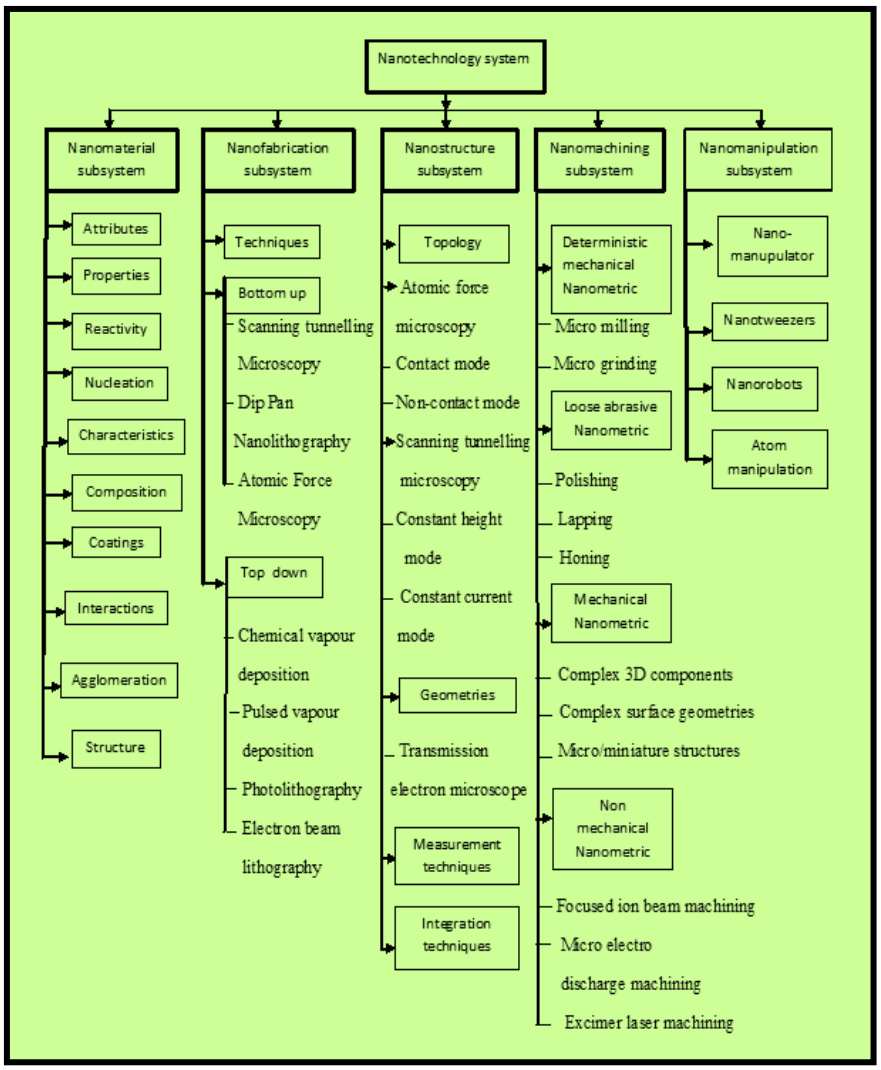

Figure-1.96.Structural constituents of nanotechnology system.

These constituents are connected with each other through different forms of bonding and interactions. The constituents and interactions forming a composite are shown in **Figure-1.97.**with the help of a schematic diagram Blocks show constituents, lines show connectivity/interactions, and arrows show directional bonding/interactions. However, schematic diagram is a good representation of nanotechnology for better understanding its structure but it is not a mathematical entity. However it is not possible to derive different results as no mathematical operation can be carried out. It is proposed to introduce a mathematical representation of nanotechnology system (i.e. constituents cum process design and manufacturing) attributes in an attempt to develop a systems model for analysis and synthesis of the nanotechnology system which will be useful to carry out analysis of an existing product for improvement and cost reduction apart from other benefits in the competitive world. **[198,199].** A nanotechnology may be considered to be a system [N, I] of its constituents set [N] = [N_1,N_2,.....Nn] and interactions/connectivity set [I] = [I_1,I_2,.....I_n] , where N_i represents ith constituent (and attributes associated with it) while I_j represents jth interactions/connectivity between two corresponding constituents of the nanotechnology.

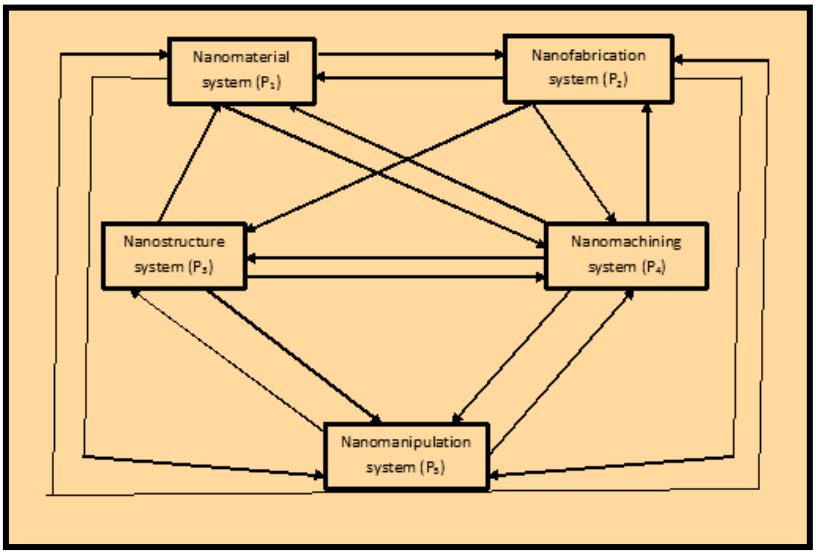

Figure-1.97.Schematic representation of the structure of nanotechnology system

For the systems representation of the nanotechnology, it is quite logical to select graph theory **[198]** and for the mathematical representation of a nanotechnology structural system diagram shown in **Figure-1.97** it would be logical to select matrix algebra **[200].** A graph G is a set if vertex and edge [V, E] where vertex set [V] = [V_1, V_2, ...V_n] and edge set [E] = [e_1, e_2, ...e_m] are its subset. I n a bid to represent a nanotechnology system mathematically, let the constituents of the nanotechnology be represented by vertex set [V] of the graph and connectivity/interactions between different constituents be represented by edge set [E]. Any directional property existing in the connectivity/interactions is represented by directed edge instead of an undirected edge. To develop an algorithm, let us assume that there are five constituents [N_1,N_2,N_3,N_4,N_5] forming a nanotechnology system shown in **Figure-1.98** and these are represented by five vertices [v_1,v_2,v_3,v_4,v_5] i. e. the constituents N_i is represented by the vertex v_i. .

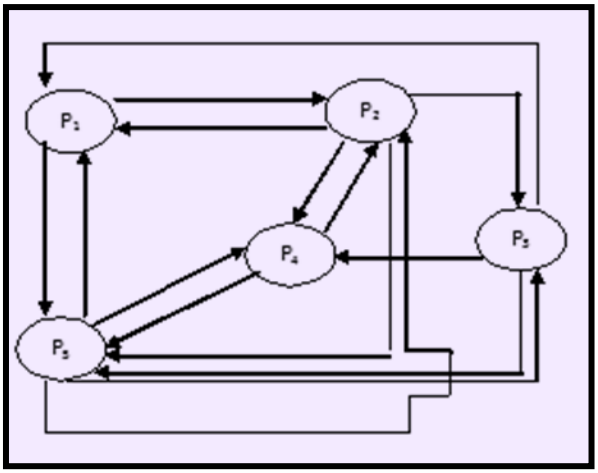

Figure-1.98. Nanotechnology system digraph

Let any connectivity/interactions existing between the constituents N_i and N_j , i.e. between v_i and v_j be represented by the edge e_{ij} (an edge existing between v_i and v_j). If we assume that all the five constituents are interacting with each other and have general directional characteristics, the nanotechnology system has a graph theoretic representation with eij ≠ $e_{ji.}$ The $e_{ij} \neq e_{ji}$ means that the influence of the ith vertex on jth vertex is not equal to the influence of jth vertex on ith vertex. If the directional property is not significant, the nanotechnology system is represented by an undirected graph, in this case $e_{ij} = e_{ji.}$

In many nanotechnology systems some of the constituents are not connected or interacting with each other. In that case, no edge will exist between those vertices. In some of the nanotechnology system there is no directional interactions present between two constituents i.e. vertices these edges will be undirected while other edges will be directed. It means a graph theoretic representation of a nanotechnology system may consists of both the directed and undirected edges.

A nanotechnology system essentially consists of five subsystems (i) Nanomaterial system, (ii) Nanofabrication system, (iii) Nanostructure system, (iv) Nanomachining system, (v) Nanomanipulation system. The influence of one subsystem over the other subsystem is also shown schematically in **Figure-1.97**.The nanomaterial subsystem affects the nanomanipulation system, while reverse also influences but it's less significant. The schematic diagram shown in **Figure-1.97** which is a non mathematical entity, is now represented by a mathematical entity called as nanotechnology system digraph is shown in **Figure-1.98** (digraph representation of the structure of nanotechnology system) .If we do not consider directional interactions i.e. $P_{ij}=P_{ji}$ then undirected graph representation of the nanotechnology system is given in **Figure-1.99**. Its permanent function is written as Equation (6) and the graphical representation of different terms is shown in **Figure-2.**The five subsystems shown in the figure above gives only the integration/connectivity. One way or two way interactions and the degree of influence are not considered in the undirected graph because of $P_{ij}=P_{ji}$.

4.4.1. Matrix representation

Since a digraph is a visual representation, it helps in visual analysis to a limited extent only. To establish a computer friendly representation for nanotechnology system, the digraph is represented in matrix form, which is convenient in computer processing also**. [196].**

The undirected graph representation of the nanotechnology system is given in **Figure-1.99.** The matrix representation permits to carry out storage, retrieval and analysis of nanotechnology systems

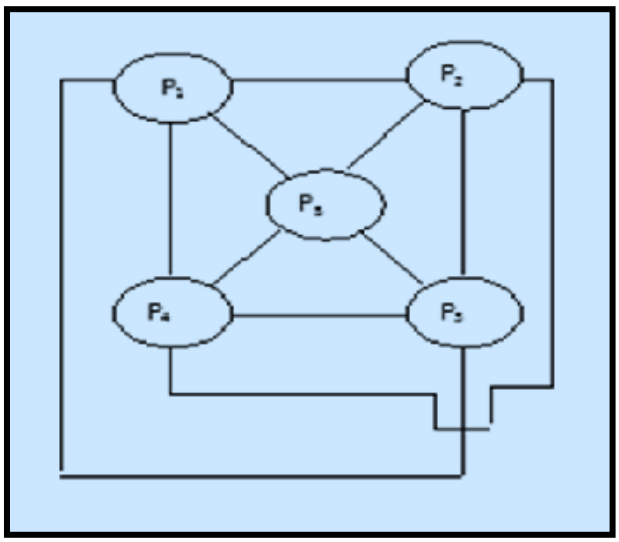

Figure-1.99. Undirected graph representation of the structure of nanotechnology system

Let us represent a digraph of 'n' subsystems leading to an nth-order symmetric (0,1) matrix A= [P_{ij}]. The rows and columns in the matrix represent the vertices/subsystems attributes, i.e. P_{ij} represents the interactions of the ith subsystem with the jth subsist

P_{ij} = 1, if subsystem i is connected to subsystem j.
0, otherwise

Generally $P_{ij} \neq P_{ji}$ as nanotechnology attributes are directional and $P_{ii} = 0$, as a subsystem is not interacting with itself (sometimes if can exist, for the moment let us assume it does not exist). The nanotechnology system matrix is square and non symmetric and is analogous to the adjacency matrix in graph theory. The nanotechnology system matrix (NTSM) representing the digraph shown in **Figure-1.98** is written as:-

$$A = \begin{array}{c} \begin{matrix} 1 & 2 & 3 & 4 & 5 & \text{Vertex} \end{matrix} \\ \begin{bmatrix} 0 & 1 & 0 & 1 & 1 & 1 \\ 1 & 0 & 1 & 1 & 1 & 2 \\ 1 & 0 & 0 & 1 & 1 & 3 \\ 1 & 1 & 1 & 0 & 1 & 4 \\ 1 & 1 & 1 & 1 & 0 & 5 \end{bmatrix} \end{array} \quad \text{..... (1)}$$

In the above matrix A, the values of P_{ii}, P_{13}, P_{32} are zero by assumption. Off diagonal elements with value 0 and 1 represents the interdependency and connectivity between subsystems Pi, i=1,2,3.....,5 of the nanotechnology system. The diagonal elements are 0

because there is no interdependency/connectivity of any subsystem with itself. To characterize the nanotechnology system, a characterize matrix is defined.

4.4.1.1. Nanotechnology System Characteristic Matrix (CM-NANOTECHNOLOGY)

Let us consider an identity matrix I, and P as the variable representing the composite system. The characteristics matrix already used in mathematics **[200]** is used to characterize the nanotechnology system. The nanotechnology system characteristics matrix, B, for the digraph shown in **Figure-1.98**, may be expressed as [PI-A], where A is the NSM represented in Equation (1)

$$B = \begin{array}{c} \begin{array}{ccccc} 1 & 2 & 3 & 4 & 5 \end{array} \\ \begin{bmatrix} P & -1 & 0 & -1 & -1 \\ -1 & P & -1 & -1 & -1 \\ -1 & 0 & P & -1 & -1 \\ -1 & -1 & -1 & P & -1 \\ -1 & -1 & -1 & -1 & P \end{bmatrix} \end{array} \begin{array}{c} \text{Vertex} \\ 1 \\ 2 \\ 3 \\ 4 \\ 5 \end{array}$$

..... (2)

In the above matrix B, the value of all diagonal elements is the same (i.e. all nanotechnology subsystems are assumed to be identical which may or may not be true in practice, since all nanotechnology subsystems have different characteristics depending on various parameters affecting them). Interdependencies between the subsystems have been assigned values of 0 and 1 depending on whether it is there or not. This does not represent varying degree of influence of one subsystem over the other subsystems. To consider this, another matrix called the nanotechnology system variable characteristics matrix is proposed.

4.4.1.2. Nanotechnology System Variable Characteristics Matrix (VCM-NANOTECHNOLOGY)

The nanotechnology system variable characteristics matrix takes into consideration the effect of different nanotechnology subsystems and their varying degrees of interactions. The digraph in **Figure-1.98** is considered for defining VCM-NANOTECHNOLOGY. Let P_is and P_{ij}s represent nodes and edges, respectively in the digraph. Consider a square matrix C with off diagonal elements P_{ij} representing varying interactions between the nanotechnology subsystems, i.e., instead of 1 (as in the matrix of Equation (1)). Another matrix D is taken with diagonal elements P_i , i = 1,2,3,4.5 where the P_i represents five different subsystems as shown in **Figure-1.97**.As these are distinct systems, P_i will represent varying inheritance of structural attributes in these subsystems. Considering matrices C and D, VCM-NANOTECHNOLOGY is expressed as H = [D-C]

The below matrix H, permits us to represent complete information about all the five subsystems and interactions amongst them. This information is useful for analysis, design, and development of new nano product at conceptual stage or for optimization purposes. The matrix provides a powerful tool through its determinant, called the variable characteristics nanotechnology multinomial (VC-NANOTECHNOLOGY).

This is a characteristic of the system and represents the complete nanotechnology system, considering the effect of nanotechnology subsystems and their interactions. Due to consideration of selective interactions between the nanotechnology subsystems (as per **Figure-1.98**), some of the diagonal elements in the matrix, H, i.e.in Equation (3), are zero.

$$H = \begin{array}{c} \begin{matrix} 1 & 2 & 3 & 4 & 5 & \text{Vertex} \end{matrix} \\ \begin{bmatrix} P_1 & 0 & 0 & 0 & 0 \\ 0 & P_2 & 0 & 0 & 0 \\ 0 & 0 & P_3 & 0 & 0 \\ 0 & 0 & 0 & P_4 & 0 \\ 0 & 0 & 0 & 0 & P_5 \end{bmatrix} \end{array} \begin{matrix} 1 \\ 2 \\ 3 \\ 4 \\ 5 \end{matrix} \quad \text{..... (3)}$$

The determinant of the matrix, H, i.e. the variable characteristics nanotechnology multinomial, carries positive and negative signs with some of its terms. The multinomial, in the symbolic terms, contains complete information of the nanotechnology system. If we replace symbols P_i and P_{ij} with their numerical values, information will be lost. Hence complete information in the nanotechnology system will not be obtained as some will be lost due to the addition and subtraction of numerical values of the diagonals and off diagonal elements (i.e. P_is and P_{ij}s). Thus the multinomial of the matrix H in Equation (3) does not provide complete information concerning the nanotechnology system under certain conditions.

To avoid the loss of structural information during mathematical processing, another term nanotechnology system variable permanent matrix (VPM-NANOTECHNOLOGY) is introduced

4.4.1.3. Nanotechnology System Variable Permanent Matrix (VPM-NANOTECHNOLOGY)

To develop a unique and comprehensive model of nanotechnology system represented by a schematic diagram (**Figure-1.97**) and a digraph (**Figure-1.98**), another entity permanent and permanent matrix, frequently used in combinational mathematics is proposed. Let the permanent matrix of five-subsystem of nanotechnology system be defined as

$$P = \begin{array}{c} \begin{matrix} 1 & 2 & 3 & 4 & 5 & \text{Vertex} \end{matrix} \\ \begin{bmatrix} P_1 & P_{12} & P_{13} & P_{14} & P_{15} \\ P_{21} & P_2 & P_{23} & P_{24} & P_{25} \\ P_{31} & P_{32} & P_3 & P_{34} & P_{35} \\ P_{41} & P_{42} & P_{43} & P_4 & P_{45} \\ P_{51} & P_{52} & P_{53} & P_{54} & P_5 \end{bmatrix} \end{array} \begin{matrix} 1 \\ 2 \\ 3 \\ 4 \\ 5 \end{matrix} \quad \text{..... (4)}$$

This is a most general matrix representation modelled as five-subsystem nanotechnology system. Thus, the variable permanent nanotechnology matrix (VPM-NANOTECHNOLOGY)

corresponding to the five subsystems as shown in digraph (**Figure-1.98**) is given by VPM-NANOTECHNOLOGY as in Equation (5), The diagonal elements P_1, P_2, P_3, P_4, P_5, represents the contribution of the five critical subsystems in producing a nanotechnology system and the off diagonal elements represents interdependences of subsystem in the matrix

This model permits the representation of the contribution of each subsystem and interaction quantitatively without any loss of information in multinomial representation.

$$E = \begin{array}{c} \begin{matrix} 1 & 2 & 3 & 4 & 5 & \text{Vertex} \end{matrix} \\ \begin{bmatrix} P_1 & P_{12} & 0 & P_{14} & P_{15} \\ P_{21} & P_2 & P_{23} & P_{24} & P_{25} \\ P_{31} & 0 & P_3 & P_{34} & P_{35} \\ P_{41} & P_{42} & P_{43} & P_4 & P_{45} \\ P_{51} & P_{52} & P_{53} & P_{54} & P_5 \end{bmatrix} \begin{matrix} 1 \\ 2 \\ 3 \\ 4 \\ 5 \end{matrix} \end{array} \quad \text{..... (5)}$$

4.4.2. Permanent function representation

Both digraph and matrix representation are not unique as these models change by changing the labelling of nodes. To develop a unique representation of nanotechnology system, independent of labelling, a permanent function of the matrix VPM-NANTECHNOLOGY is proposed for this purpose. Permanent is a standard matrix function and is used in combinational mathematics **[200, 201].**

The permanent function is obtained from a matrix in a similar manner as its determinant. A negative sign appears in the expansion of determinant while in the permanent, i.e. the variable permanent function, positive signs replace these negative signs. This computation process result in a multinomial (Equation (6)) that's every term has a physical significance related to the nanotechnology system. This multinomial representation includes all the information regarding various constituents as subsystems, sub-subsystems, and interactions amongst them. The variable permanent function for a nanotechnology system modelled as five subsystem nanotechnology system can be derived from matrix representation shown in Equation (4).

The variable permanent function for a nanotechnology system is

$$\begin{aligned} \text{per}(P) = {} & P_1P_2P_3P_4P_5 + (P_1P_2P_3P^2_{45} + P_1P_2P_4P^2_{35} + P_1P_2P_5P^2_{34} + P_1P_3P_4P^2_{25} + P_1P_3P_5P^2_{24} \\ & + P_1P_4P_5P^2_{23} + P_2P_3P_4P^2_{15} + P_2P_3P_5P^2_{14} + P_2P_4P_5P^2_{13} + P_3P_4P_5P^2_{12}) + (2P_1P_2P_{34}P_{45}P_{53} \\ & + 2P_1P_3P_{24}P_{45}P_{52} + 2P_1P_4P_{23}P_{35}P_{52} + 2P_1P_5P_{23}P_{34}P_{42} + 2P_3P_4P_{12}P_{25}P_{51} + 2P_3P_5P_{12}P_{24}P_{41} \\ & + 2P_2P_3P_{14}P_{45}P_{51} + 2P_2P_5P_{13}P_{34}P_{41} + 2P_2P_4P_{13}P_{35}P_{51} + 2P_4P_5P_{12}P_{23}P_{31}) + (P_1P^2_{23}P^2_{45} \\ & + P_1P^2_{24}P^2_{35} + P_1P^2_{25}P^2_{34} + P_2P^2_{45}P^2_{13} + P_2P^2_{14}P^2_{35} + P_2P^2_{15}P^2_{34} + P_3P^2_{12}P^2_{45} + P_3P^2_{14}P^2_{25} \\ & + P_3P^2_{15}P^2_{24} + P_4P^2_{12}P^2_{35} + P_4P^2 1_3P^2_{25} + P_4P^2_{15}P^2_{23} + P_5P^2_{12}P^2_{34} + P_5P^2_{13}P^2_{24} + P_5P^2_{14}P^2_{23}) \\ & + (2P_1P_{23}P_{35}P_{54}P_{42} + 2P_1P_{23}P_{34}P_{45}P_{52} + 2P_1P_{24}P_{43}P_{35}P_{52} + 2P_2P_{13}P_{34}P_{45}P_{51} \\ & + 2P_2P_{14}P_{43}P_{35}P_{51} + 2P_2P_{13}P_{35}P_{54}P_{41} + 2P_3P_{12}P_{24}P_{45}P_{51} + 2P_3P_{14}P_{42}P_{25}P_{51} \end{aligned}$$

$+2P_3P_{12}P_{25}P_{54}P_{41}$ $+2P_4P_{12}P_{23}P_{35}P_{51}+2P_4P_{13}P_{32}P_{25}P_{51}+2P_4P_{12}P_{25}P_{53}P_{31}$

$+2P_5P_{13}P_{32}P_{24}P_{41}+2P_5P_{12}P_{23}P_{34}P_{41}+2P_5P_{13}P_{34}P_{42}P_{21})$ +

$(2P^2_{12}P_{34}P_{45}P_{53}+2P^2_{13}P_{24}P_{45}P_{52}$

$+2P^2_{14}P_{23}P_{35}P_{52}$ $+2P^2_{15}P_{23}P_{34}P_{42}+2P^2_{23}P_{14}P_{45}P_{51}+2P^2_{24}P_{13}P_{35}P_{51}+2P^2_{25}P_{13}P_{34}P_{41}$

$+2P^2_{34}P_{12}P_{25}P_{51}+2P^2_{35}P_{12}P_{24}P_{41}+2P^2_{45}P_{12}P_{23}P_{31}+2P_{12}P_{23}P_{35}P_{54}P_{41}+2P_{12}P_{23}P_{34}P_{45}P_{51}$

$+2P_{12}P_{24}P_{45}P_{53}P_{31})$ + $(2P_{12}P_{24}P_{43}P_{35}P_{51}+2P_{12}P_{25}P_{53}P_{34}P_{41}+2P_{12}P_{25}P_{54}P_{43}P_{31}$

$+2P_{13}P_{32}P_{24}P_{45}P_{51}+2P_{13}P_{34}P_{42}P_{25}P_{51}+2P_{13}P_{35}P_{52}P_{24}P_{41}+2P_{13}P_{32}P_{25}P_{54}P_{41}$

$+2P_{14}P_{42}P_{23}P_{35}P_{51}+2P_{15}P_{52}P_{23}P_{34}P_{41})$ ..... (6a)

The above equation is for a general nanotechnology system modelled for five subsystems, which contains 120 terms. But the permanent function for the matrix equation (5) corresponds to **Figure-1.98**, reduces to 78 terms, because the variables P_{13} and P_{32} values are 0 which means interactions are absent.

The variable permanent function for a nanotechnology system is

per (E) $=P_1P_2P_3P_4P_5 + (P_1P_2P_3P_{45}P54+P_1P_2P_5P_{34}P_{43}+P_1P_2P_4P_{35}P_{53}+P_1P_3P_5P_{24}P_{42}$

$+P_1P_3P_4P_{25}P_{52}+P_3P_4P_5P_{12}P_{21}+P_2P_3P_5P_{14}P_{41}+P_2P_3P_4P_{15}P_{51}) + (P_1P_2P_{34}P_{45}P_{53}$

$+P_1P_2P_{35}P_{54}P_{43}+P_1P_3P_{24}P_{45}P_{52}+P_1P_3P_{25}P_{54}P_{42}+P_3P_5P_{12}P_{24}P_{41}+P_3P_5P_{14}P_{42}P_{21}$

$+P_2P_3P_{14}P_{45}P_{51}+P_2P_3P_{15}P_{54}P_{41}+P_3P_4P_{15}P_{52}P_{21}+P_3P_4P_{12}P_{25}P_{51}+P_1P_5P_{23}P_{34}P_{42}$

$+P_1P_4P_{23}P_{35}P_{52}+P_4P_5P_{12}P_{12}P_{23}P_{31}+P_2P_5P_{14}P_{43}P_{31}+P_2P_4P_{15}P_{53}P_{31}) + (P_1P_{24}P_{42}P_{35}P_{53}$

$+P_1P_{25}P_{52}P_{34}P_{43}+P_3P_{12}P_{21}P_{45}P_{54}+P_4P_{35}P_{53}P_{12}P_{21}+P_2P_{14}P_{41}P_{35}P_{53}+P_3P_{14}P_{41}P_{25}P_{52}$

$+P_2P_{15}P_{51}P_{34}P_{43}+P_3P_{15}P_{51}P_{34}P_{43}+P_3P_{15}P_{51}P_{24}P_{42}+P_5P_{12}P_{21}P_{34}P_{43}) + (P_1P_{24}P_{43}P_{35}P_{52}$

$+P_1P_{25}P_{53}P_{34}P_{42}+P_1P_{23}P_{34}P_{45}P_{52}+P_1P_{23}P_{35}P_{54}P_{42}+P_2P_{15}P_{53}P_{34}P_{41}+P_2P_{14}P_{43}P_{35}P_{51}$

$+P_2P_{14}P_{45}P_{53}P_{31}+P_2P_{15}P_{54}P_{43}P_{31}+P_3P_{12}P_{24}P_{45}P_{51}+P_3P_{15}P_{54}P_{42}P_{21}+P_3P_{14}P_{42}P_{25}P_{51}$

$+P_3P_{15}P_{52}P_{24}P_{41}+P_3P_{12}P_{25}P_{54}P_{41}+P_3P_{14}P_{45}P_{52}P_{21}+P_4P_{12}P_{23}P_{35}P_{51}+P_4P_{12}P_{25}P_{53}P_{31}$

$+P_4P_{15}P_{52}P_{23}P_{31}$ + $P_5P_{12}P_{23}P_{34}P_{41}+P_5P_{12}P_{24}P_{43}P_{31}+P_5P_{14}P_{42}P_{23}P_{31}) + (P_{12}P_{21}P_{34}P_{45}P_{53}$

$+P_{12}P_{21}P_{35}P_{54}P_{43}$ $+P_{35}P_{53}P_{12}P_{24}P_{41}+P_{35}P_{53}P_{14}P_{42}P_{21}+P_{34}P_{43}P_{12}P_{25}P_{51}+P_{34}P_{43}P_{15}P_{52}P_{21}$

$+P_{45}P_{54}P_{12}P_{23}P_{31}+P_{14}P_{41}P_{23}P_{35}P_{52}+P_{15}P_{51}P_{23}P_{34}P_{42}$ $+P_{25}P_{52}P_{14}P_{43}P_{31}+P_{24}P_{42}P_{15}P_{53}P_{31})$

$+ (P_{12}P_{24}P_{43}P_{35}P_{51}+P_{15}P_{53}P_{34}P_{42}P_{21}+P_{12}P_{25}P_{53}P_{34}P_{41}+P_{14}P_{43}P_{35}P_{52}P_{21}+P_{12}P_{23}P_{34}P_{45}P_{51}$

$+P_{12}P_{23}P_{35}P_{54}P_{41}+P_{12}P_{24}P_{45}P_{53}P_{31}+P_{12}P_{25}P_{54}P_{43}P_{31}+P_{14}P_{45}P_{52}P_{23}P_{31}+P_{14}P_{42}P_{23}P_{35}P_{51}$

$+P14P42P25P53P31+P_{15}P_{54}P_{42}P_{23}P_{31}+P_{15}P_{52}P_{23}P_{34}P_{41}+P_{15}P_{52}P_{24}P_{43}P_{31})$. ..... (6b)

The above equation uniquely represents the nanotechnology system of **Figure-1.97**.Every term of these equations represents a subset of the nanotechnology system

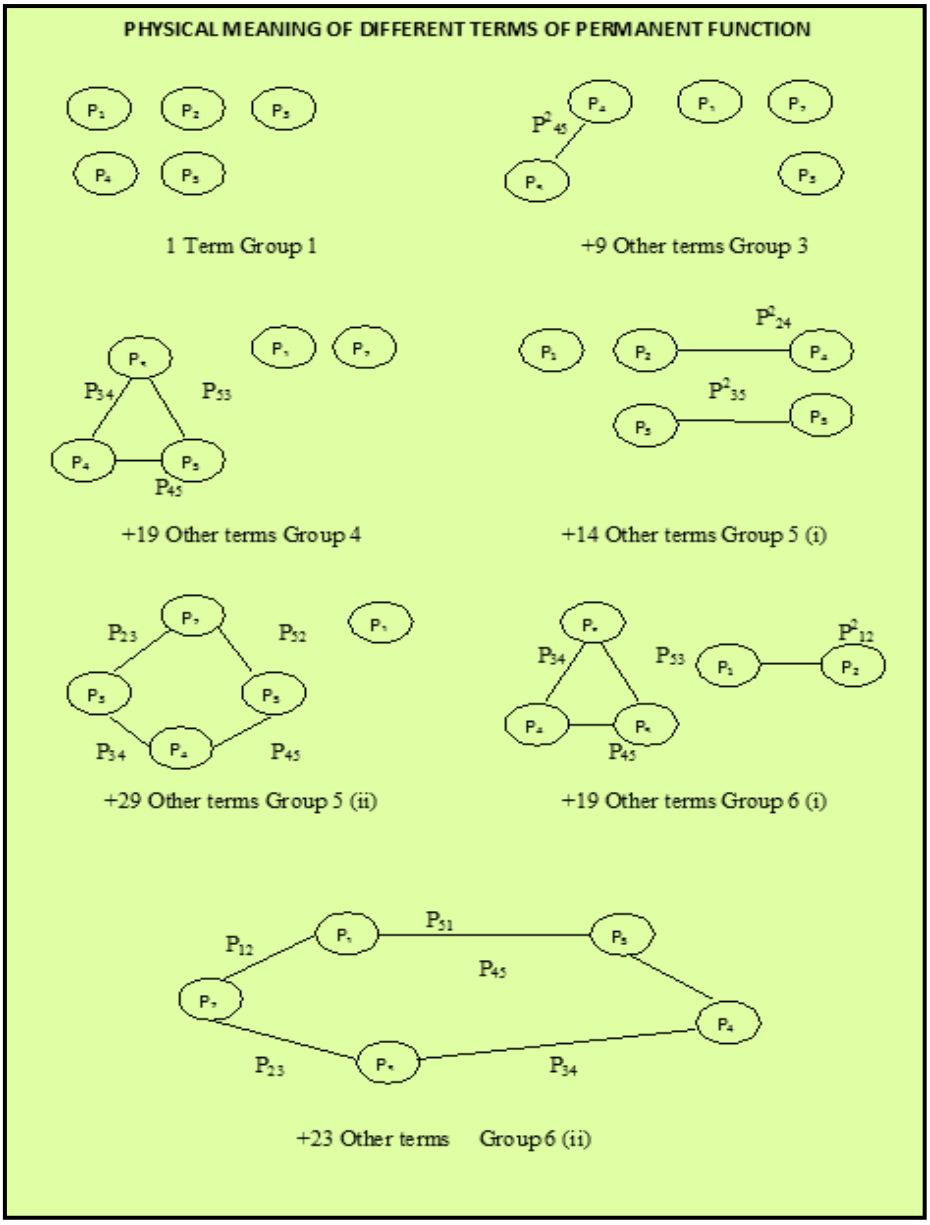

Figure-2. Graphical representation of permanent function (Equation (6)) for nanotechnology system corresponds to undirected graph (Figure-1.99)

It is possible to write these equations simply by visual inspection of the nanotechnology system of **Figure-1.98**. To achieve this objective, the permanent function of Equation (6) is written in a standard form as (N+1) groups. All these distinct combinations of subsystems and interactions of the macro system are shown graphically in **Figure-2**.

The multinomial, i.e., the permanent function when written in (N+1) groups, presents an exhaustive way of analysis of a nanotechnology at different levels. It helps in identifying different constituents, process parameters, design attribute and the interactions among various subsystems of nanotechnology systems.

Group 1 contains only one term of five isolated vertices P_is i.e. five subsystems are to be considered together as independent entities.

Group 2 is absent as a particular subsystem has no interactions with itself.

Group 3 has ten terms, each term is a set of one dyad, P^2_{ij} or a two subsystem loop i.e. P_{ij} P_{ij} and three independent subsystems (dyad is a system of two subsystems i and j, considered as one entity).

Group 4 has 20 terms in all. Each term has a set of one 3-subsystem loop and independent subsystems. The three subsystem loop is a system, to be considered as one entity.

Group 5 has two subgroups: Group 5(i) has fifteen terms; each term is a subset of two independent dyads or two-subsystem loops and one independent subsystem. Group 5 (ii) has thirty terms; each term is a set of 4-subsystem loop and one independent subsystem.

Group 6 has again two subsystems: Group 6 (i) has one 3-subsystem loop and a dyad or two-subsystem loop while Group 6 (ii) has twenty-four 5-subsystem loops.

In all, a general 5-subsystem permanent function will have 5!, i.e. 120 terms arranged in (N+1) groups. **Figure-2** gives graphical interpretation for visual understanding, analysis, and improvement of a nanotechnology system. It is therefore possible for the designer as well as the manufacturer to carry out SWOT (Strength-weakness-opportunities-threats) analysis of their complete nanotechnology system and take strategic decisions to their advantage as per policy.

4.4.2.1. Evaluation of P_i

The diagonal elements of the matrix in Equation (5) correspond to the five subsystems that constitute a nanotechnology system. The values of these diagonal elements P_1, P_2, ...P_5 are calculated as:-

P_1 = per (E P_1); P_2 = per (E P_2); P_3 = per (E P_3); P_4 = per (E P_4); P_5 = per (EP_5);

Where E P_1, E P_2, E P_3, E P_4, EP_5 are the variable permanent matrices for five subsystems of the nanotechnology system. The procedure for calculating P_1, P_2, P_3, P_5 is the same as for calculating per (E) of Equation (6a). For this purpose, the subsystems of nanotechnology system are considered, and the procedure given below is followed:

1. The schematics of these subsystems are drawn separately by considering their various sub-subsystems.
2. Identifying the degree of interactions, interconnections, dependencies, connectivity, etc, between different subsystems.

Digraph representations (like **Figure-1.98**) of five subsystems are drawn first separately to obtain their matrix equations (like Equation (5)) i.e. EP_is and their permanent functions P_is, i=1, ...5. The off diagonal terms P_{ij} (i, j=1, 2,....., 5) of matrix Equation (5) gives the connections between the systems P_i and P_j. Depending upon the type of structural analysis, P_{ij} can be represented as multinomial , graph matrix or by some analytical model. To get the exact degree of interactions, interconnections, dependencies, connectivity etc, between subsystems or sub-subsystems we may have to consider the views of technical term experts. A team of experts selected from design, manufacturing, chemistry, material science etc, to consider all the issues involved from the point of view of engineering, science, technology, and business strategy. The final decision on the values of P_is and P_{ij}s may be taken on the recommendation of the team. Thus by following the top- down approach and the step-by-step procedure given below gives the complete structural analysis of the nanotechnology system.

4.5. Analysis of Nanotechnology System

4.5.1. Nanotechnology system analysis

The methodology described in the previous sections for complete analysis of a nanotechnology system is summarized below:-

Step 1: Consider the desired nanotechnology system based on working area. Study the complete nanotechnology system and its subsystem (nanomaterial, nanofabrication, nanostructure, nanomachining, naomanipulation) and also their interactions.

Step 2: Develop a block diagram of the nanotechnology system, considering its subsystems and interactions along with assumptions, if any.

Step 3: Develop a system graph of the nanotechnology with subsystem as nodes and edges for interconnection between the nodes (See **Figure-1.98** for details).

Step 4: Develop the matrix and multinomial representations of nanotechnology system See **Figure-1.97** for details).

Step 5: Evaluate functions/values of diagonal elements from the permanent functions of distinct subsystems of the nanotechnology and repeat step 2-4 for each subsystem.

Step 6: Identify the functions/values of off diagonal elements/interconnections at different levels of hierarchy of the nanotechnology that is systems, subsystems, sub-subsystems etc.

The values (or functions) of interactions P_{ij} (i, j = 1, 2, 3, N) between different subsystems P_1, P_2,..... P_N can be written as a multinomial or a matrix, depending upon the type of interaction/reaction between the two subsystems. The sub-subsystems can again be treated as systems, as every sub-subsystem is a system in itself. Following the above procedure, these subsystems can be broken down into sub-subsystems and different graph, matrix, and permanent representations can be obtained. Depending upon the depth of analysis required, the process could be taken to the constituent level and further. In certain cases, it may be possible to evaluate P_{ij}'s experimentally or using available mathematical models. With the help of this data, complete multinomial for the nanotechnology system can be evaluated. Work is in progress to carry out performance analysis of any nanotechnology system from different perspectives using the structural model is presented.

4.5.2. Generalization of the model

The variable permanent function (VPF) being the characteristic of nanotechnology system for any industrial product is a powerful tool for its analysis. The VPF-NANOTECHNOLOGY system expression which corresponds to the five-factor digraph is written in a compact sigma ($\sum$) form as VPF-NANOTECHNOLOGY

$$= \text{per (E)} = \prod_1^5 + \sum_i \sum_j \sum_k \sum_l \sum_m . (P_{ij} P_{ji}) P_k P_l P_m + \sum_i \sum_j \sum_k \sum_l \sum_m . (P_{ij} P_{jk} P_{ki} + P_{ik} P_{kj} P_{ji}) P_l P_m + (\sum_i \sum_j \sum_k \sum_l \sum_m . (P_{ij} P_{jk}) (P_{kl} P_{lk}) P_m + \sum_i \sum_j \sum_k \sum_l \sum_m . ((P_{ij} P_{jk} P_{kl} P_{li}) + (P_{il} P_{lk} P_{kj} P_{ji})) P_m) + \sum_i \sum_j \sum_k \sum_l \sum_m . (P_{ij} P_{ji} (P_{kl} P_{lm} P_{mk} + P_{km} P_{ml} P_{lk}) + \sum_i \sum_j \sum_k \sum_l \sum_m . (P_{ij} P_{jk} P_{kl} P_{lm} P_{mi} + P_{im} P_{ml} P_{lk} P_k \quad \ldots . \quad (7)$$

The above equation is a generalised mathematical expression in symbolic form corresponding to five-factor digraph representation. It ensures an estimate of the nanotechnology system of any industrially fabricated product. The above equation contains 5! Terms. Each term is

useful for a nanoproduct designer as each term serves as a test for the effectiveness of the relevant group in per (E). Equation (7) contains terms arranged in (N+1) groups, where N is the number of subsystems, which in this case are 5. The physical significance of various grouping is explained as follows:

1. The first term (grouping) represents a set of N unconnected nanotechnology subsystems, i.e. $P_{1,}$ $P_{2,.....}$ $P_{N.}$
2. The second grouping is absent in the absence of self loops.
3. Each term of the third grouping represents a set of two-element nanotechnology system loops (i.e. $P_{ij,}$ $P_{ji,)}$ and is the resultant nanotechnology system dependence of characteristics i and j and the nanotechnology system measure of the remaining (N-2) unconnected elements.
4. Each term of the fourth grouping represents a set of three-element nanotechnology subsystem interaction loops (P_{ij} $P_{jk}P_{ki}$ or its pair $P_{ik}P_{kj}P_{ji}$) and the nanotechnology system measure of the remaining (N-3) unconnected elements.
5. The fifth grouping contains two subgroups. The terms of the first sub grouping consists of two-element composite subsystem interaction loops (i.e. $P_{ij}P_{ji}$ and $P_{kl}P_{lk}$) and nanotechnology constituent $P_{m.}$ The terms in the second grouping are a product of four-element nanotechnology subsystem interaction loops (i.e. $P_{ij}P_{jk}P_{kl}P_{li}$) or its pair (i.e. $P_{il}P_{lk}P_{kj}P_{ji}$) and nanotechnology constituent P_{m} .
6. The terms of the sixth grouping are also arranged in two sub groupings. The terms of the first sub grouping are a product of a two-element nanotechnology subsystem interaction loop (i.e. $P_{ij}P_{ji}$) and a three-element nanotechnology subsystem interaction loop (i.e. $P_{kl}P_{lm}P_{mk}$) or its pair (i.e. $P_{km}P_{ml}P_{lk}$). The second sub grouping consists of a five-component nanotechnology subsystem interaction loop (i.e. $P_{ij}P_{jk}P_{kl}P_{lm}P_{mi}$) or its pair (i.e. $P_{im}P_{ml}P_{lk}P_{kj}P_{ji}$).

4.6. Generalization of present methodology

Suppose a system consists of N subsystems and is represented as a digraph, then the most general way of matrix representation is shown below.

This matrix is also known as the variable permanent matrix (VPM) corresponding to the N subsystems

1	2	3	.	.	N	Components
P1	P12	P13	.	.	P1N	1
P21	P2	P23	.	.	P2N	2
P31	P32	P3	.	.	P3N	3
.	.	.	.	.	.	.
.	.	.	.	.	.	.
.	.	.	.		.	.
.	.	.	.	.	.	.
.	.	.	.	.	.	.
.	.	.	.	.	.	.
.	.	.	.	.	.	.
.	.	.	.	.	.	.
PN1	PN2	PN3	.	.	PN	N

..... (8)

Permanent for the above matrix, i.e. per (E) is called variable permanent function (VPF). The VPF for the above matrix is written in sigma form as

per (E) = $\prod_{a=1}^{N} + \sum_i \sum_j \sum_k \ldots \ldots \ldots \sum_N . (P_{ij} P_{ji}) P_k P_l \cdots P_N + \sum_i \sum_j \sum_k \ldots \ldots \ldots \sum_N . (P_{ij} P_{jk} P_{ki}$

$+P_{ik}P_{kj}P_{ji})P_lP_m \cdots P_N+(\sum_i \sum_j \sum_k \ldots \ldots \ldots \sum_N .(P_{ij}P_{jk})(P_{kl}P_{lk})P_mPn \cdots P_N+$
$\sum_i \sum_j \sum_k \ldots \ldots \ldots \sum_N . (P_{ij}P_{jk}P_{kl} P_{li}) + (P_{il} P_{lk} P_{kj} P_{ji})) P_mPn \cdots P_N) + (\sum_i \sum_j \sum_k \ldots \ldots \ldots \sum_N .(P_{ij}$
$P_{ji})(P_{kl} P_{lm} P_{mk} + P_{km} P_{ml} P_{lk}) Pn Pa \cdots P_N + \sum_i \sum_j \sum_k \ldots \ldots \ldots \sum_N . (P_{ij} P_{jk} P_{kl} P_{lm} P_{mi} + P_{im} P_{ml}$
$P_{lk} P_{kj} P_{ji}) Pn Po \cdots P_N) + \cdots$ ..... (9)

The number and composition of groups and subgroups will be the same as discussed earlier. So it is possible to write the permanent function of any nanotechnology system. It may be noted that a permanent function will contain N! Terms only, provided P_{ij}s are not 0. In certain cases, designer and/or manufacturer team may decide that some of P_{ij}s are 0. Substitution of corresponding P_{ij}s equal to 0 in general permanent function (Equation (9)) or in general VPM (Equation (8)) gives the exact number of terms with modified permanent function.

4.7. Comparison

A nanotechnology system is represented as a system consisting of five subsystems, which affects properties and performance of final system. This five-subsystem nanotechnology is modelled as a multinomial, a permanent function. Different nanotechnology system based on different areas will have a different number of terms in different groups and subgroups of their permanent functions. The similarity or dissimilarity between any nanotechnology systems is obtained by comparing their permanents. Using the proposed methodology, the identification of a nanotechnology system and its comparison with other nanotechnology system is based on the analysis carried out with the help of VPF-NANOTECHNOLOGY. Two nanotechnology systems are similar from subsystems and its interactions viewpoint if their digraph is isomorphic. Two nanotechnology systems digraph are isomorphic if they have identical VPF-NANOTECHNOLOGY. This means that not only the number of terms in each grouping/sub-grouping is the same but also that the values are the same.

Based on this, a nanotechnology system identification set for any system is written as:

$[(J^P_1/J^P_2/J^P_3/J^P_4/J^P_{51}/J^P_{52}/J^P_{61}/J^P_{62}/.....) (V^P_1/V^P_2/V^P_3/V^P_4/V^P_{51}+V^P_{52}/V^P_{61}+V^P_{62}/.....)]$ ..... (10)

Where J^P_i represents the total number of terms in the ith grouping. J^P_{ij} represents the total number of terms in the jth grouping. In case there is no sub grouping, the J_{ij} is the same as J^P_i similarly V^P_i is the value of the ith grouping. V^P_{ij} is the numerical values of the P_is and P_{ij}s are substituted in the sub grouping or grouping to obtain $V^P_{ij.}$ The sub groupings are arranged in decreasing order of size (i.e. number of elements in a loop).In general; two nanotechnology systems may not be isomorphic from the viewpoint of interactions among subsystems. A comparison is also carried out on the basis of the coefficient of similarity. The coefficient is derived from the structure, i.e. VPF-NANOTECHNOLOGY and compares two nanotechnology systems or a set of nanotechnology systems on the basis of similarity or dissimilarity. If the value of distinct terms in the jth subgrouping of the ith grouping of VPF-NANTECHNOLOGY of two nanotechnology systems under consideration is denoted by V^P_{ij} and V'^P_{ij} , then two criteria are proposed as follows:

Criterion 1: The coefficient of dissimilarity C^P_{d-1} based on Criterion 1 is proposed as

$$C^P_{d-1} = \frac{1}{Y_1 \sum_i \sum_j \emptyset ij} \quad \text{..... (11)}$$

Where,

$$Y_1 = \max \left(\sum_i \sum_j [V^P_{ij}] \text{ and } \sum_i \sum_j V'^P_{ij}] \right)$$

When sub groupings are absent $V_{ij} = V^P_i$ and $V'^P_{ij} = V'^P_i$ and $\phi_{ij} = [V^P_{ij} - V'^P_i]$, when the sub grouping exists and $\phi_{ij} = [V^P_i - V'^P_i]$, when the subgrouping are absent.

Criterion 2: The coefficient of dissimilarity C^P_{d-2} based on Criterion 2 is proposed as

$$C^P_{d-2} = \left[1 \Big/ Y_1 \sum_i \sum_j . \phi^2 ij \right] 1/2 \quad \text{..... (12)}$$

Where $\phi_{ij\ is}$ same as described above and

$$Y_2 = \max \left(\sum_i \sum_j . \ (V^P_{ij})^2 \text{ and } \sum_i \sum_j .(V'^P_{ij})^2 \right)$$

When sub groupings are absent $V_{ij} = V^P_i$ and $(V'^P_{ij}) = V'^P_{i,}$ using Equations (11) and (12), the coefficient of similarity is given as

$$C^P_{s-1} = 1 - C^P_{d-1}; \quad C^P_{s-2} = 1 - C^P_{d-2}$$

Where C^P_{s-1} and C^P_{s-2} are the coefficients of similarity between two nanotechnology system under consideration based on criterion 1 and 2. It may be noted that the coefficient of similarity and dissimilarity lie in the range between 0 and 1, if two nanotechnology systems are isomorphic or completely similar, their coefficient of similarity is 1 and the coefficient of dissimilarity is 0. In a similar manner, if two nanotechnology systems are completely dissimilar, their coefficient of similarity is 0 and the coefficient of dissimilarity is 1.

4.8. Concluding Remarks

The methodology is dynamic in nature as constituents and bonding may be changed without any difficulty. The approach helps to express the nanotechnology system in quantitative terms, which has more often been expressed in qualitative terms. The procedure also helps to compare different nanotechnology systems in terms of its characteristics and rate them for a particular application. It is hoped that this methodology will provide a new direction in the research attempts towards global projects of quantitative structure activity relationship (QSAR) and quantitative structure properties relationship (QSPR) **[196]** The present work is an attempt towards the development of complete methodology for virtual fabrication **[197]** of nanoproducts as well as virtual design of complete nanotechnology system consisting of nanomaterial, nanofabrication, nanostructure, nanomaching and nanomanipulation

CHAPTER-5

ATTRIBUTE BASED CODING, EVALUATION AND OPTIMUM SELECTION OF NANOMATERIAL

"MADM Approach"

This chapter deals with implementing a novel method to help the decision-maker for selection of a proper material that will meet all the requirements of the design engineers in this reliable and exhaustive data of nanomaterial is to generate and maintain based on their different pertinent attributes. It is useful for better understanding, comparison and analysis and for comparison; ranking and optimum selection of nanomaterial from a large number of nanomaterial available in global market, the multiple attribute decision making problems is solved by "TOPSIS" (Technique for Order Preferences by Similarity to Ideal Solution). The techniques convert database into knowledge base by considering normalization, relative weights, positive benchmarked and negative benchmarked solutions and normalized weighted database into single numerical suitability index for each candidate nanomaterial solution. It helps the nanomaterial user to save time by providing a tool for selecting the nanomaterial most suited for his operational needs. The selection procedure allows rapid convergence from large number of candidate nanomaterial to a manageable shortlist of potentially suitable nanomaterial using elimination search based on the few critical selection attributes. Subsequently, the selection procedure proceeds to rank the alternatives in the shortlist by employing different attributes based specification and graphical methods. The ranks of the candidate nanomaterial are calculated with respect to the best possible nanomaterial, say +ve benchmark nanomaterial, for particular application. The coding scheme and the selection procedures, mathematical and graphical, with example are also illustrated

5.1. Introduction

Nanomaterial is those materials where the size of the individual building block is less than 100nm at least in one dimension. Nanomaterial means any intentionally produced material that has one or more dimensions of the order of 100nm or less or is composed of discrete functional parts, either internally or at the surface, many of which have one or more dimensions of the order of 100nm or less, including structures, agglomerates or aggregates, which have a size above the order of 100nm but retain properties that are characteristic to the nanoscale. Recent developments in design, the selection of nanomaterial play an important role for engineers. The nanomaterial selection should not be solely based on cost but also depends on different properties of nanomaterial, availability, recycling, production method, disposal method, design life, etc. Selection of nanomaterial depends on number of attributes or factors. Hence, selection of nanomaterial is a multi attribute decision-making problem. Selection of the appropriate nanomaterial is an integral part of successfully implementation of an engineer's design. The ability to select the most appropriate nanomaterial for a given application is the fundamental challenges faced by the design engineer. A multi attribute

analysis is a popular tool to select best alternative for given applications and the methods are simple additive weighted (SAW) method, weighted product method (WPM), technique for order preference by similarity to ideal solution (TOPSIS), Vlse Kriterijumska Optimizacija Kompromisno Resenje (VIKOR) method, analytical hierarchy process (AHP), graph theory and matrix representation approach (GTMA) etc. Nanomaterial selection is one of the most challenging issues in the design and development of structural elements and it is also critical the success and competitiveness of the manufacturing organisation. Thus, great efforts need to be extended to determine attributes that influence nanomaterial selection, using a simple logical approach, to eliminate unsuitable nanomaterial and selection of a proper nanomaterial to be strengthen the existing nanomaterial selection procedure. The selection of an optimal nanomaterial for an engineering design from among various alternatives based on different attributes (i.e. subjective, objective) can be defined within the concept of a multiple attribute decision-making (MADM) problem. There has been rapid increase in the number of nanomaterial and nanomaterial manufacturers. Nanomaterial with vastly different capabilities and specifications are available for a wide range of applications. The selection of the nanomaterial to suit a particular application and production environment, from the large number of nanomaterial available in the market today has become a difficult task. Various considerations such as availability, recycling, production method, disposal method, design life need to be considered before a suitable nanomaterial be selected.

5.2. Novel Methodology

MADM techniques are product selection techniques. Multiple attributes are processed in MADM techniques for ranking finite number of alternatives to arrive at a single choice for the best product. This article uses Technique for Order Preferences by Similarity to Ideal Solution (TOPSIS) MADM technique to select a best possible nanomaterial. The weighted normalized attributes for the +ve and _ve benchmark nanomaterial are considered as attributes for arriving at best possible nanomaterial to deploy in the application considered which having required ability.

Step-by-step procedure for optimum selection of nanomaterial

Step-1:- Decide about the aims and objective for which nanomaterial is to be used.

Step-2:-Identify all the possible alternative nanomaterial available in the literature.

Step-3:-Use cause and effect diagram to find out different classes/groups of attributes/properties/characteristics and different attributes in identified classes.

Step-4:-Develop an n-digit coding scheme for characterization/specification for storage and retrieval in the computer.

Step-5:-Carry out elimination search to reduce the large list of alternatives nanomaterial as 1^{st} stage of 3^{rd} stage selection procedure.

Step-6:-Select TOPSIS (Technique for Order Preferences by Similarity to Ideal Solution) as attribute based evaluation procedure for this small list of alternatives.

Step-7:-After evaluation, rank the nanomaterial in order of preference for given application.

5.2.1. Nanomaterial attributes

Proper identification of nanomaterial attributes is critically important when comparing various Alternative nanomaterials.

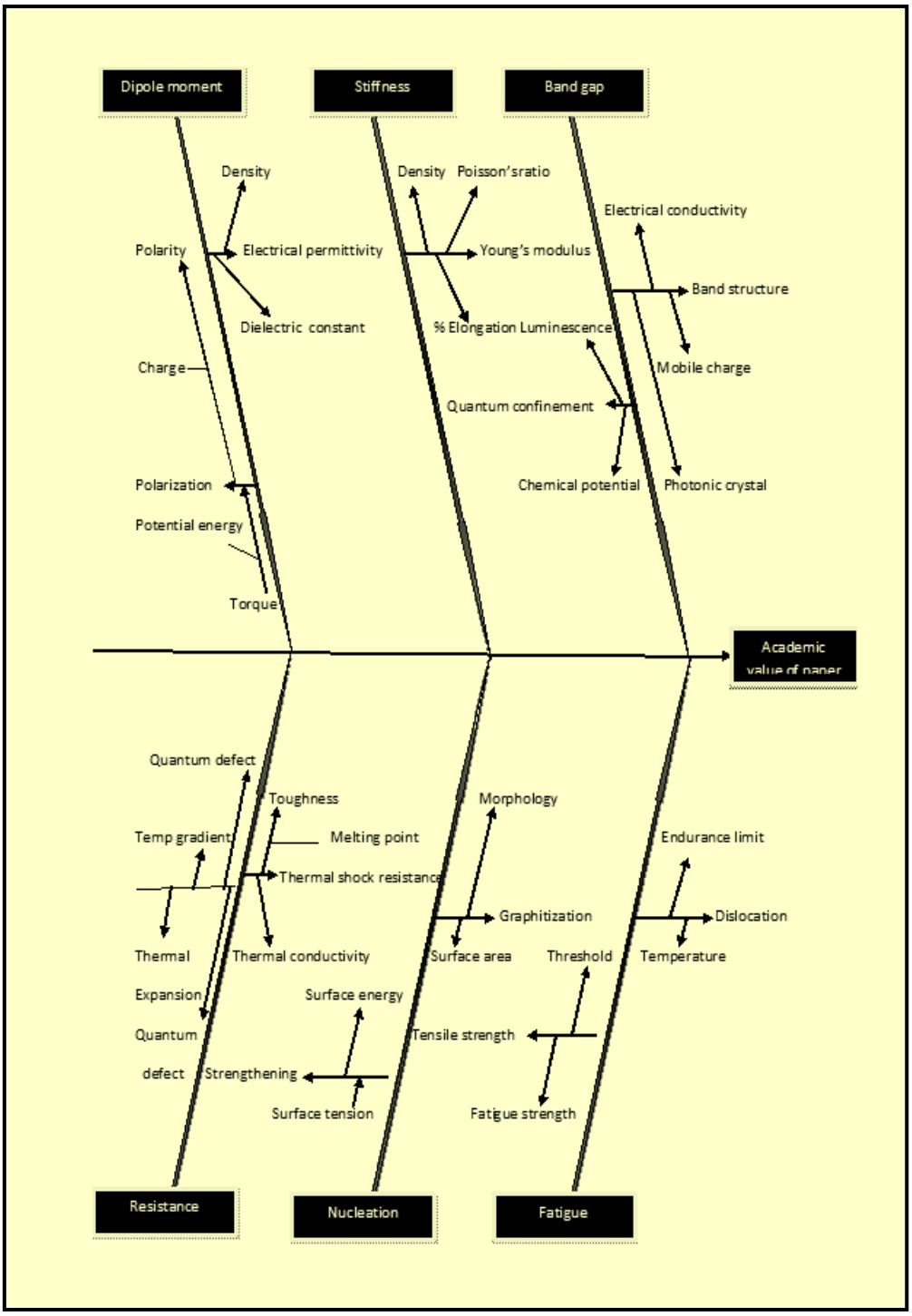

Figure-2.1. Cause and effect analysis of nanomaterial characterization.

However, in most cases the user needs to be assisted in identifying the nanomaterial attributes wisely and accordingly the application. The final product of industry directly depends on the proper choice of the nanomaterial. Cause and effect analysis diagram is drawn to identify all the different attributes and other parameters of nanomaterial which require attention/ situation of researchers in the subject area under consideration as shown in **Figure-2.1.**

5.2.1.1. Identification of Nanomaterial attributes

The nanomaterial attributes are found out based on its broad area as general parameters, physical parameters, and mechanical, atomic, electrical. Thermal based etc as shown in **Table-1.19**

General Attributes	
1. Malleability	2. Polymorphism
3. Ductility	4. Surface topology
5. Lustrous	6. Structural bond forces
7. Softness	8. Ionic distribution
9. Durability	10. Dielectric relaxation
11. Molecular weight	12. Stiffness
13. Resistance to oxidation	14. Capacitance stability
15. Resistance to corrosion	16. Granularity
17. Conductivity of electricity	18. Dimensional stability
19. Surface Plasmon resonance	20. Transparency
21. Chemical reactivity	22. Power loss factor
23. Colour	24. Point adhesion
25. Internal reflection	26. Magnetic ordering
27. Phase	28. Resistance to deformation
29. Capable of transmitting light	30. Specific surface area
31. Index of refraction	32. Crystallite size
33. Lubricity	34. Crystal phase
35. Strength	36. Reaction rate
37. Resistance to neutron radiation	38. Catalytic selectivity
39. Rigidity	40. Debye wall factor
41. Wear resistance	42. BENS broadening
43. Biocompatibility	44. Fragility
45. Film friction coefficient	46. Current density
47. Impact sensitive	48. Resistance to arcing
49. Toughness	50. Orbit hybridization
51. Dispersion	52. Metallic behaviour
53. Reinforcement	54. Aspect ratio
55. Stability	56. Radial elasticity
57. Solubility	58. Symmetry
59. Brittleness	60. Polarizability
61. Resistance to high temperature	62. Taper ratio
63. Strengthening	64. Light weight
65. Substrate	66. Ballistic resistance capacity
67. Relative chemical inertia	68. Toxicity
69. Robustness	70. Angle of incidence
71. Monoclinic	72. Electromagnetic resonance

73. Dielectric breakdown	74. Crystal structure
75. Resistance to cracking	76. Thermo ionic
	77 Work function
Physical Attributes	
78.Density	79. Platy
80.True density	81. Specific suspension
82.Melting point	83. Resilience
84.Boling point	85. Bulk density
86.Heat of fusion	87. Decomposition temperature
88.Heat of vaporization	89. Threshold electric field
90. Molar heat capacity	91. Binding energies
92. Lattice constant	93. Catalyst
94. Metallic radius	95. Curvature energies
96. Gas solid liquid	97. String tension
98. Wavelength	99. Diameter
100. Morphology	101. Particle size
102. Bond distance	103. Emissivity
104. Purity	105. Richard constant
106. Molar density	107. Hardness
108. Dielectric	109. Length
110. Hydrophilic	111. Brightness
	112. Short term beam stability
Mechanical Attributes	
113.Tensile strength	114. Compression yield strength
115. Young's modulus	116. Coefficient of friction
117. Shear modulus	118. Flexural strength
119. Bulk modulus	120. Percentage elongation
121. Poisson's ratio	122. Impact strength
123. Mohr hardness	124. Deformation stress
125. Vickers hardness	126. Van der wall forces
127. Brinell hardness	128. Internal surface area
129. Knoop hardness	130. Specific strength
	131. Fracture toughness
Atomic Attributes	
132.Oxidation states	133.Atomic radius
134.Electro-negativity	135.Covalent radius
136 Ionization energies	137.Van der wall radius
Electrical Attributes	
138. Electrical resistivity	139. Electrical performance
140. Dielectric constant	141. Superconductivity
142. Dielectric strength	143. Conductance quantization
144. Band structure	145. Band gap
146. Curvature effects	147. Electrical conductivity

Thermal Attributes	
148. Thermal conductivity	149. Thermal stability
150. Thermal expansion	151. Thermal source
152. Specific heat	153. Coefficient of thermal expansion

154. Temperature	155. Ballistic conductance
156. Standard entropy	157. Temperature stability
158. Standard enthalpy of formation	159. Phonon mean free path
160. Nucleation	161. Relaxation time
Optical Attributes	
162. Transmission	163. Absorption
164. Luminescence	165. Photo-luminescence
166. Index of refraction	167. Surface Plasmon
	168. Oscillation

Table-1.19.List of broad categories attributes of nanomaterial

The above 168 attributes is useful for storage, retrieval, designing, manufacturing, evaluation, ranking and optimum selection of nanomaterial for R & D of a nanodevice.

5.2.2. Quantification and measurement of the attributes

The nanomaterial are expressed in detailed manner with the attributes identified e.g., Young's modulus 107Gpa, Tensile strength >55Gpa, Aspect ratio 1000 etc. But all attributes are not quantitative, e.g., band structure, morphology, etc. The nanomaterial is rated on the scale of 0-5 for these attributes. A similar approach has to be used for the informative attributes, which just tell information about some attribute of the nanomaterial such as the structure of the nanomaterial or the density of nanomaterial , which is denoted by some number whose numerical value have no significance.

It cannot be used for the mathematical treatment since it is just a representation and numeric value has no significance. There are some attributes of which quantification is not readily available and has to be done by some mathematical model or modelling, simulation and analysis Quantification of many of the attributes is not readily available from the manufacturer. But if the manufacturer make it a standard practice to identify, quantify and provide these attributes, it is helpful to him apart from nanomaterial designer, user etc

a. Usefulness to the manufacturer

The quantification and monitoring of the attribute magnitudes help the manufacturer to control them closely so that he fulfils the demand of the user precisely.

Moreover, he finds out the market trend by observing the attributes magnitudes. It helps the manufacturer to modify his product to suit the future needs of the nanomaterial user. He uses the data to produce optimum nanomaterial in the minimum possible time. The nanomaterial manufacturer uses these attributes for the SWOT (Strength–Weakness–Opportunity–Threat) analysis of his nanomaterial product as shown in **Figure-2.2.**

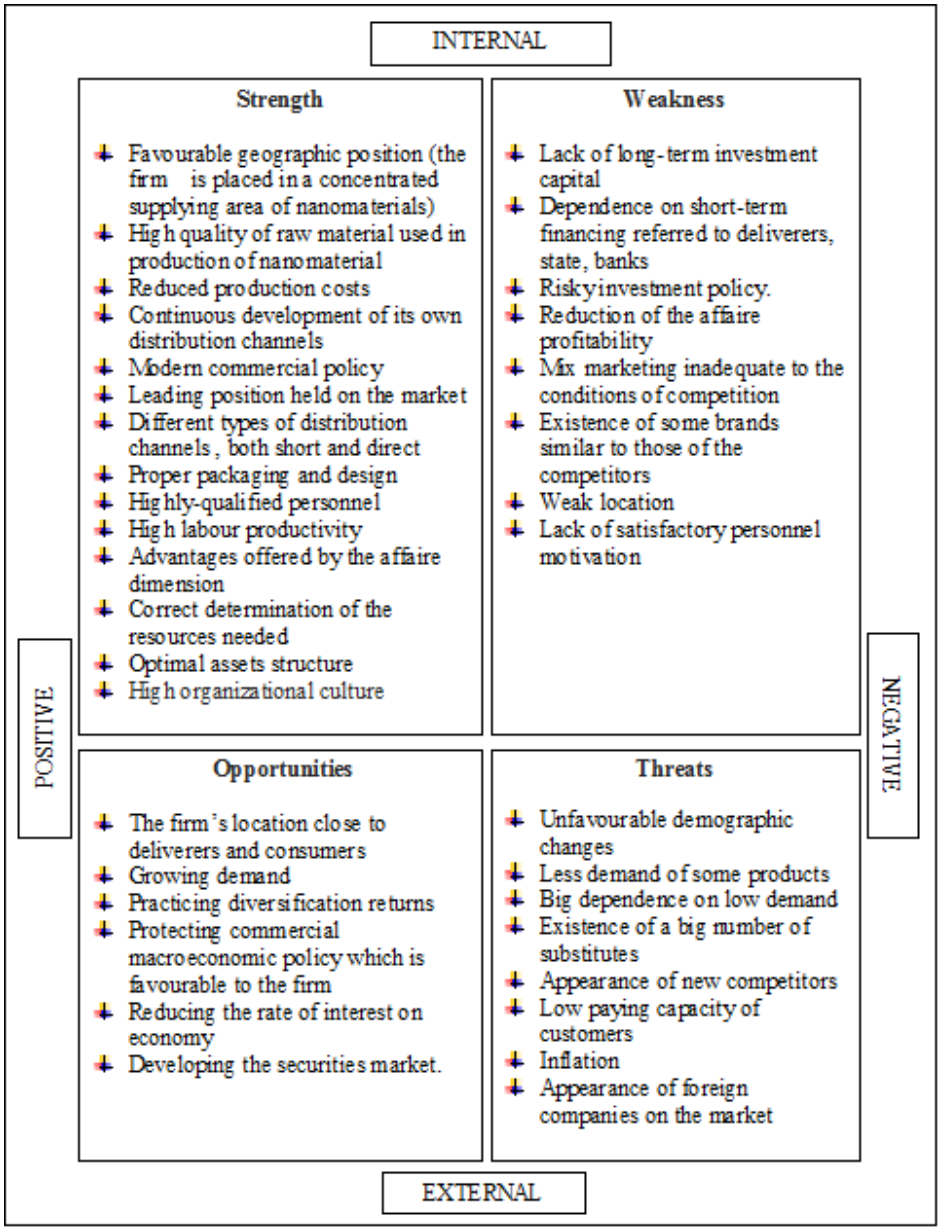

Figure-2.2.SWOT analysis for manufacturer

b. Usefulness to the designer

For the designer at conceptual design stage, identification helps to generate various alternative designs, which is developed as modular nanomaterial. Using the modular nanomaterial approach, the optimum nanomaterial according to the market requirements is designed in very little time. He identifies the critical attributes, which directly affects the performance. The designer changes these critical attributes and monitors them to control particular parameters so that the required performance obtained from the nanomaterial. Designer use these attributes for cause and effect analysis, where he find out the effects of manipulating these attributes on the nanomaterial performance.

c. Usefulness to the user

Identification of the attributes helps the user for the data storage and its retrieval. It generates the computerized data, which is used in different formats for different purposes by different people in the organization. It helps the user to select the best possible nanomaterial for the particular application whenever it is required.

Keeping the short term and long term objectives in mind, comprehensive SWOT analysis by the designer, device manufacturer and R & D organizations helps in the development of creative and innovative nanodevices.

5.2.3. Coding Scheme for Nanomaterial Attributes

In order to facilitate the selection of pertinent attributes for the application, the attributes are required to be evaluated and coded for range of values. Coding is alphanumeric. The attributes are of two types: quantitative/deterministic and qualitative/fuzzy/subjective. Quantitative attributes determined or calculated using mathematical models or experimentally.

Qualitative attributes are subjective in nature and imprecise information is available. It is desirable to evaluate the existence of both types of attributes on one of the several internal scales. E. g. 0-5 etc for uniformity. Quantification of many of these attributes is not readily available from the manufacturer. A team of experts from relevant disciplines codify all the attributes related to a particular nanomaterial. Following examples illustrative the proposed coding scheme for qualitative and quantitative attributes:-

5.2.3.1. Quantitative Attributes

Specific surface area in cm^2/g	Code
Up to 25 cm^2/g	0
50 cm^2/g	1
100 cm^2/g	2
150 cm^2/g	3
200 cm^2/g	4
250 cm^2/g and above	5

Table-1.20. Coding of specific surface area of nanomaterial

Coding of specific surface area of nanomaterial as shown in **Table-1.20**. These codes are used to specify the specific surface area of the nanomaterial in the respective shell number 30, since it is allotted to it, as shown in **Table-1.24**.

Here the nanomaterial under consideration has the specific surface area of 290 cm^2/g, which is given a code 5 as shown in **Table-1.25**.

Tensile strength in GPa	Code
Up to 10 GPa	0
20 GPa	1
30 GPa	2
40 GPa	3
50 GPa	4
60 GPa and above	5

Table-1.21.Coding of tensile strength of nanomaterial

Coding of tensile strength of nanomaterial as shown in **Table-1.21**. These codes are used to specify the tensile strength of the nanomaterial in the respective shell number 113, since it is allotted to it, as shown in **Table-1.24**. Here the nanomaterial under consideration has the tensile strength of 400GPa, which is given a code 3 as shown in **Table-1.25.**

5.2.3.2. Qualitative Attributes

Magnetic ordering	Code
Not available	0
Magnetic	1
Diamagnetic	2
Paramagnetic	3

Table-1.22.Coding of magnetic ordering of nanomaterial

Coding of magnetic ordering of nanomaterial as shown in **Table-1.22**. These codes are used to specify the magnetic ordering of the nanomaterial in the respective shell number 51, since it is allotted to it, as shown in the **Table-1.24**. Here the nanomaterial under consideration is diamagnetic in nature, which is given a code D as shown in **Table-1.25.**

Morphology	Code
Cubic	0
Body centred cubic	1
Face centred cubic	2
Cylindrical	3
Tubular	4
Pseudo hexagonal	5

Table-1.23.Coding of morphology of nanomaterial

Coding of morphology of nanomaterial as shown in **Table-1.23**. These codes are used to specify the morphology of the nanomaterial in the respective shell number 89, since it is allotted to it, as shown in the **Table-1.24**. Here the nanomaterial under consideration having tubular structure, which is given a code T as shown in **Table-1.25.**

The above mentioned attributes tabulated in the form of 168-digit coding scheme for characterization of nanomaterial as shown in **Table-1.24**.

General	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
	76	77													
Physical	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92
	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107
	108	109	110	111	112										
Mechanical	113	114	115	116	117	118	119	120	121	122	123	124	125	126	127
	128	129	130	131											
Atomic	132	133	134	135	136	137									
Electrical	138	139	140	141	142	143	144	145	146	147					
Thermal	148	149	150	151	152	153	154	155	156	157	158	159	160	161	
Optical	162	163	164	165	166	167	168								

Table-1.24.168-digit coding scheme for characterization of nanomaterial

Example of coding scheme of standard nanomaterial. "**Q Tubes® 250"** nanomaterial as shown in **Table-1.25**

S/No	**Attributes**	**Information**	**Code**
1	Malleability	-	0
2	Polymorphism	None	N
3	Ductility	-	0
4	Surface topology	-	0
5	Lustrous	-	0
6	Structural bond forces	-	0
7	Softness	-	0
8	Ionic distribution	-	0
9	Durability	-	0
10	Dielectric relaxation	-	0
11	Molecular weight	-	0
12	Stiffness	-	0
13	Resistance to oxidation	-	0
14	Capacitance stability	-	0
15	Resistance to corrosion	-	0
16	Granularity	-	0
17	Conductivity of electricity	-	0
18	Dimensional stability	Stable	4
19	Surface Plasmon resonance	-	0
20	Transparency	-	0

21	Chemical reactivity	-	0
22	Power loss factor	-	0
23	Colour	Black	B
24	Point adhesion	-	0
25	Internal reflection	-	0
26	Magnetic ordering	Diamagnetic	D
27	Phase	-	0
28	Resistance to deformation	-	0
29	Capable of transmitting light	-	0
30	Specific surface area	290 m^2/g	5
31	Index of refraction	-	0
32	Crystallite size	-	0
33	Lubricity	-	0
34	Crystal phase	Specific Phase Amorphous Highly Crystalline	A
35	Strength	-	0
36	Reaction rate	-	0
37	Resistance to neutron radiation	-	0
38	Catalytic selectivity	-	0
39	Rigidity	-	0
40	Debye wall factor	-	0
41	Wear resistance	-	0
42	BENS broadening	-	0
43	Biocompatibility	-	0
44	Fragility	-	0
45	Film friction coefficient	-	0
46	Current density	$>3.2x10^9 A/cm^2$	5
47	Impact sensitive	-	0
48	Resistance to arcing	-	0
49	Toughness	-	0
50	Orbit hybridization	-	0
51	Dispersion	Soluble in Organic Solvents	3
52	Metallic behaviour	-	0
53	Reinforcement	-	0
54	Aspect ratio	~1000	5
55	Stability	Stable	S
56	Radial elasticity	-	0
57	Solubility	Insoluble	IS
58	Symmetry	-	0
59	Brittleness	-	0
60	Polarizability	-	0
61	Resistance to high temperature	-	0
62	Taper ratio	-	0
63	Strengthening	-	0
64	Light weight	-	0
65	Substrate	-	0
66	Ballistic resistance capacity	-	0
67	Relative chemical inertia	-	0
68	Toxicity	-	0
69	Robustness	-	0

70	Angle of incidence	Amorphous highly Crystalline	5
71	Monoclinic	-	0
72	Electromagnetic resonance	-	0
73	Dielectric breakdown	-	0
74	Crystal structure	-	0
75	Resistance to cracking	-	0
76	Thermo ionic	-	0
77	Work function	-	0
78	Density	-	0
79	Platy	-	0
80	True density	~2.1g/cm^3	4
81	Specific suspension	Dispersions in Organic Solvents	W
82	Melting point	3652-3697 Degree C	5
83	Resilience	-	0
84	Boling point	-	0
85	Bulk density	0.20g/cm^3	5
86	Heat of fusion	-	0
87	Decomposition temperature	-	0
88	Heat of vaporization	-	0
89	Threshold electric field	-	0
90	Molar heat capacity	-	0
91	Binding energies	-	0
92	Lattice constant	-	0
93	Catalyst	Slight Impurities < 5% Trace catalyst	3
94	Metallic radius	-	0
95	Curvature energies	-	0
96	Gas solid liquid	Physical State Solid Amorphous Powder	P
97	String tension	-	0
98	Wavelength	-	0
99	Diameter	Average Outer Diametre12nm, Average Inner Diameter 8nm	5
100	Morphology	Seamless and Fracture less Tubular Structure	T
101	Particle size	-	0
102	Bond distance	-	0
103	Emissivity	-	0
104	Purity	>95% by weight	4
105	Richard constant	-	0
106	Molar density	-	0
107	Hardness	-	0
108	Dielectric	-	0
109	Length	4-5 micrometer	4
110	Hydrophilic	-	0
111	Brightness	-	0
112	Short term beam stability	-	0
113	Tensile strength	>55GPa	4
114	Compression yield strength	-	0
115	Young's modulus	107 GPa	5

116	Coefficient of friction	-	0
117	Shear modulus	-	0
118	Flexural strength	-	0
119	Bulk modulus	-	0
120	Percentage elongation	-	0
121	Poisson's ratio	-	0
122	Impact strength	-	0
123	Mohr hardness	-	0
124	Deformation stress	-	0
125	Vickers hardness	-	0
126	Van der wall forces	0.2cm	2
127	Brinell hardness	-	0
128	Internal surface area	-	0
129	Knoop hardness	-	0
130	Specific strength	-	0
131	Fracture toughness	-	0
132	Oxidation states	-	0
133	Atomic radius	-	0
134	Electro-negativity	-	0
135	Covalent radius	-	0
136	Ionization energies	-	0
137	Van der wall radius	-	0
138	Electrical resistivity	-	0
139	Electrical performance	Conducting	C
140	Dielectric constant	-	0
141	Superconductivity	-	0
142	Dielectric strength	-	0
143	Conductance quantization	-	0
144	Band structure	-	0
145	Band gap	-	0
146	Curvature effects	-	0
147	Electrical conductivity	>100 Simens/cm (Along Tube Axis)	5
148	Thermal conductivity	>3000 w/m/k (Along Tube Axis)	5
149	Thermal stability	-	0
150	Thermal expansion	-	0
151	Thermal source	-	0
152	Specific heat	-	0
153	Coefficient of thermal expansion	-	0
154	Temperature	-	0
155	Ballistic conductance	-	0
156	Standard entropy	-	0
157	Temperature stability	2800 Degree C in Vaccum and 780 Degree C in Air	4
158	Standard enthalpy of formation	-	0
159	Phonon mean free path	-	0
160	Nucleation	-	0
161	Relaxation time	-	0
162	Transmission	-	0
163	Absorption	-	0

164	Luminescence	-	0
165	Photo-luminescence	-	0
166	Index of refraction	-	0
167	Surface Plasmon	-	0
168	Oscillation	-	0

Table-1.25.coding scheme for standard nanomaterial

Here, coding scheme for all the 168 attributes are shown for standard nanomaterial under consideration. All these attributes for **"Q Tubes® 250"** nanomaterial is collected from different research publications and some of them from commercial products and applications.. Table clearly indicates that the information supplied by the manufacturer to the user is meagre and it is required to be more elaborate. Here that most of the cells are having 0 as code in them. The 0 represents that the information relating to the particular cell is not available to the authors. Information is not provided by the manufacturer, but the authors think that if this information is provided it makes the data exhaustive.

General	0	N	0	0	0	0	0	0	0	0	0	0	0	0	0
	0	0	4	0	0	0	0	B	0	0	D	0	0	0	5
	0	0	0	A	0	0	0	0	0	0	0	0	0	0	0
	5	0	0	0	0	3	0	0	5	S	0	IS	0	0	0
	0	0	0	0	0	0	0	0	0	5	0	0	0	0	0
	0	0													
Physical	0	0	4	W	5	0	0	5	0	0	0	0	0	0	0
	3	0	0	P	0	0	5	T	0	0	0	4	0	0	0
	0	4	0	0	0										
Mechanical	4	0	5	0	0	0	0	0	0	0	0	0	0	2	0
	0	0	0	0											
Atomic	0	0	0	0	0	0									
Electrical	0	C	0	0	0	0	0	0	0	5					
Thermal	5	0	0	0	0	0	0	0	0	4	0	0	0	0	
Optical	0	0	0	0	0	0	0								

Table-1.26.Representation of coding scheme for standard nanomaterial

Moreover, the data storage, retrieval and the selection procedure more precise and accurate. Representation of coding scheme for standard nanomaterial **"Q Tubes® 250"** can be done for all 168 attributes as shown in **Table-1.26**.

The alphabets used in the coding scheme for standard nanomaterial has unique information in itself , like , here material that we are taken for comparison purpose is of black colour represented by letter 'B' similarly, it is stable in nature represented by 'S', it is insoluble in nature represented by 'IS', polymorphism is not done represented by 'N', magnetic ordering of material is diamagnetic in nature represented by 'D' having a amorphous crystal phase represented by 'A' and physical in nature represented by 'P', morphology of tubular structure represented by 'T', specific suspension is dispersion in water represented by 'W', having electrical performance of conducting in nature represented by 'C'. Rest of numerical codes are given on the basis of their relative importance highest code i.e. '5' to highly important attribute and lesser code like '4', and '3' to less important and '2', 'and 1' to very less important attribute and '0' for totally absent attribute. This coding scheme is also used for the visual comparison between two nanomaterials up to certain extent. It allows faster comparison in various formats.

5.3. 3-Stage Optimum Selection Procedure

5.3.1. Stage-1 Elimination Search Method

Though all the attributes have been identified, all of them would not be important while selecting the nanomaterial for particular application. There are few attributes, which have direct effect on the selection procedure. The small number of attributes set-aside as 'pertinent attributes' as necessitated by the particular application and/or the user. The threshold values to these 'pertinent attributes' assigned by obtaining information from the user and the group of experts. Henceforth the selection procedure focuses solely on the pertinent attributes leaving out the rest. On the basis of the threshold values of the pertinent attributes, a shortlist of nanomaterial is obtained. It is achieved by scanning the data for pertinent attributes, one at a time, to eliminate the nanomaterial alternatives, which have one or more pertinent attribute values that fall short of the minimum required (threshold) values. To facilitate that search procedure an identification system has been made for all the nanomaterial in the data.

5.3.2. Stage-2 Evaluation using TOPSIS Method

5.3.2.1. Decision matrix

The first step here to represent all the information available from the data about these satisfying solutions in the matrix form. Such a matrix is called as decision matrix, D. Each row of the matrix is allocated to one candidate nanomaterial and each column to one attribute under consideration. Therefore an element d_{ig} of the decision matrix D, gives the value of jth attribute in the row (non-normalized) form and units, for the ith nanomaterial. Thus if the number of short-listed nanomaterial is 'm' and the number of pertinent attributes is 'n' the decision matrix is an m x n matrix.

5.3.2.2. Step-2 Normalized specifications

The second step is construction of the normalized specification matrix, N, from the decision matrix, D. Normalization is used to bring the data within particular range or scale, and moreover it provides the dimensionless magnitudes. The phenomenon is used to calculate the normalized specification matrix. The normalized specification matrix has the magnitudes of all the attributes of the nanomaterial on the common scale of 0 to 1. It is a sort of value, which indicates the standing of that particular attribute magnitude when compared to the whole range of the magnitudes for all candidate nanomaterial.
An element n_{ij} of the normalized matrix N be calculated as:-

$$n_{ij} = d_{ij} \Big/ \left(\sum_{i=1}^{m} d_{ij}^2 \right)^{1/2} \quad \text{..... (1)}$$

Where d_{ij} is an element of the decision matrix, D.

The next step is to obtain information from the user or the group of experts on the relative importance of one attribute with respect to another. The information is sought in terms of a ratio. Information on all such pair-wise comparisons is stored in a matrix called as relative importance matrix, 'A', which is n x n matrix. Here a_{ij} contain the relative importance of i^{th} attribute over the j^{th} attribute. The symmetric terms of the matrix are reciprocals of each other while the diagonal be unity. The information stored in a matrix is on pair-wise basis. It is to be modified into representation that gives the relative weights of all attributes taken together so that the cumulative sum of the weights is equal to unity. The Eigen vector method seeks to find weight vector w from the Eigen value problem associated with the matrix, A, i.e.

$$A\,x = \lambda x \quad \text{..... (2)}$$

Where λthe Eigen value of A and x is is the corresponding Eigen vector **[134].** For n x n A there are n Eigen values λ_i, for i = 1,. . .,n, and corresponding to λ_i, there are n Eigen vectors x_i, for i = 1,. . .,n. vector w is now found in the following manner:

1. Take Eigen vector, x_{max} corresponding to the largest Eigen value λ_{max}, as all the elements of x_{max} are either positive or negative.

2. Find the sum of the elements of x_{max} as

$$\alpha = \sum_{i=1}^{n} (\mathbf{x}_i)_{\max} \quad \text{..... (3)}$$

3. Find weight vector w as

$$\mathbf{w} = (\mathbf{x}_{\max})/\alpha \text{ such that } \sum_{i=1} \mathbf{w}_i = 1. \quad \text{..... (4)}$$

5.3.2.3. Step-3 Weighted normalized specification

The weights obtained from the relative importance matrix have to be applied to the normalized specifications since all attributes have different importance while selecting the nanomaterial for particular application. The matrix, which combines the relative weights and normalized specification of the candidates, is weighted normalized matrix, 'V'. It gives the true comparable values of the attributes. This is obtained as follows:

$$\mathbf{V} = \begin{bmatrix} w_1 n_{1,1} & w_2 n_{1,2} & \cdots & w_n n_{1,n} \\ w_1 n_{2,1} & \ddots & \cdots & \vdots \\ \vdots & \vdots & \ddots & \vdots \\ w_1 n_{m,1} & w_2 n_{m,2} & \cdots & w_n n_{m,n} \end{bmatrix} = \begin{bmatrix} v_{1,1} & v_{1,2} & \cdots & v_{1,n} \\ v_{2,1} & \ddots & \cdots & \vdots \\ \vdots & \vdots & \ddots & \vdots \\ v_{m,1} & v_{m,2} & \cdots & v_{m,n} \end{bmatrix}$$

..... (5)

5.3.2.4. Stage -3 Ranking and Optimum Selection Procedure

The ranking of the nanomaterial done by either mathematically (TOPSIS method) or graphically (Line graph and Spider diagram methods).

5.3.2.4.1. TOPSIS method

The weighted normalized matrix V is used to obtain the +ve and -ve benchmark nanomaterial, where the both benchmark nanomaterial are hypothetical nanomaterial, which supposed to have best and worst possible attribute magnitudes. The TOPSIS method is based on the concept that the chosen option (optimum) have the shortest distance from the +ve benchmark nanomaterial (best possible nanomaterial) and be farthest from the _ve benchmark nanomaterial (worst possible nanomaterial). The measure ensures that the top ranked nanomaterial is closest to +ve benchmark nanomaterial and farthest from _ve benchmark nanomaterial. Here, calculations are made on separation measures from +ve and _ve benchmark nanomaterial, respectively, as S_i^* and S_i^-

The separation from the +ve benchmark nanomaterial is given by

$$S_i^* = \left[\sum_{j=1}^{n} (v_{ij} - v_1^*)^2\right]^{1/2} \quad (i = 1, 2, \ldots, m) \qquad \text{..... (6)}$$

And separation from the -ve benchmark nanomaterial is given by

$$S_i^- = \left[\sum_{j=1}^{n} (v_{ij} - v_1^-)^2\right]^{1/2} \quad (i = 1, 2, \ldots, m) \qquad \text{..... (7)}$$

Then the relative closeness to the +ve benchmark nanomaterial, C*, which is a measure of the suitability of the nanomaterial for the chosen application on the basis of attributes considered, is calculated. A nanomaterial with the largest C* is preferable.

$$C^* = S_i^- / (S_i^* + S_i^-) \quad \text{..... (8)}$$

Ranking of the candidate nanomaterial in accordance with the decreasing values of indices C* indicating the most preferred and the least preferred feasible optional solutions is done.

5.3.2.4.2. Graphical methods

Till now have been seen the mathematical representation of the specifications, normalized and weighted normalized specifications. There are many methods to evaluate the nanomaterial using mathematical approach **[135].** But trying to explore graphical way to process the available data and select the nanomaterial. The graphical representation methods like line graph used for that purpose.

5.3.2.4.2.1. Line graph representation

We have specification matrix D, normalized and weighted normalized specification matrices N and V, respectively, containing information of the candidate nanomaterial. These matrices represented graphically using line graph by plotting the magnitude of the attributes on the vertical axis and the attributes on the horizontal axis. Please note that the attributes, of which minimum values are preferred. If the values are plot for different candidate nanomaterial, obtain the line graph for them. These graphs distinct for all of the candidate nanomaterial and used as comparison basis. The area under the curve used to quantification purpose and to compare the candidate nanomaterial with each other and benchmark nanomaterial is shown in **Figure-2.3**

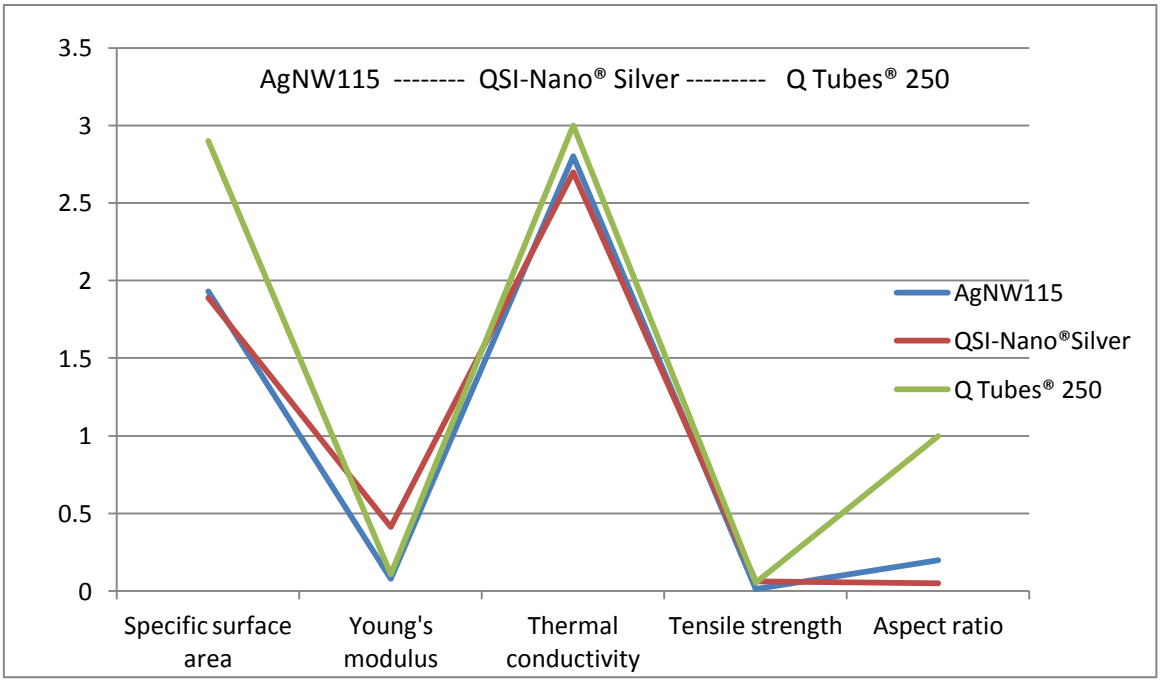

Figure-2.3.line graph plot for the specifications and the area under the curve is shaded.

These line graphs plotted for specifications, normalized and weighted normalized specifications of all the candidate nanomaterial as well as the benchmark nanomaterial. The area under the curve obtained as follows. Let the width between the two parameters on horizontal axis as unity and d_{ij}, n_{ij}, and v_{ij} are the elements of D, N, and V matrices.

Area under the line graph of specification of ith nanomaterial found out as:-

$$AD_i^L = (d_{i,1} + 2(d_{i,2} + \cdots + d_{i,n-1}) + d_{i,n})/2 \quad \text{..... (9)}$$

Similarly, area under the graph of normalized and weighted normalized specifications of the ith nanomaterial, i.e. AN_i^L and AV_i^L using their respective elements.

5.3.2.4.3. Identification and graphical representation of the benchmark nanomaterial.

The same +ve benchmark nanomaterial, defined earlier, is used here for the comparison of the candidate nanomaterial for the ranking purpose. The areas under the line graph for +ve benchmark nanomaterial, i.e., $AD^L_{B,}$ $AN^L_{B,}$ and AV^L_B are calculated. All the candidate nanomaterial compared with the +ve benchmark nanomaterial for the evaluation purpose. It shows the suitability of the nanomaterial for the particular task.

5.3.2.4.4. Ranking and selection of the nanomaterial

Now specification matrix is there along with normalized specification and weighted specification matrices ready for all the candidate nanomaterial along with the +ve benchmark nanomaterial. There is a need to measure and to compare the candidates with benchmark nanomaterial so that be ranked and selected.

5.3.2.4.5. Coefficient of similarity (COS).

The evaluation and ranking of the nanomaterial using the novel graphical methods done by their similarity to +ve benchmark nanomaterial. Let the Coefficient of similarity (COS) is the ratio of area under the curve or enclosed by the polygon for the candidate to that of the benchmark nanomaterial. The value of COS be any +ve fraction ($0 \leq COS \leq 1$) and a measure of the closeness of candidate nanomaterial with the benchmark nanomaterial. The candidates with COS magnitude closer to unity are preferable, since it indicates the closeness to the +ve benchmark nanomaterial.

Coefficient of similarity (COS) based on decision matrix

$$COS_J^D = AD_J/AD_I \quad \text{..... (10)}$$

AD_j for jth nanomaterial and different methods, i.e., line graph, etc.

Coefficient of similarity (COS) based on normalized specifications matrix

$$COS_j^N = AN_j/AN_I \quad \text{..... (11)}$$

AN_j for jth nanomaterial and different methods, i.e., line graph, etc.

Coefficient of similarity (COS) based on weighted normalized matrix

$$COS_j^I = AV_j / AV_I$$ ..... (12)

AV_j for jth nanomaterial and different methods, i.e., line graph, etc.

Thus the COS calculations for all the n number of candidate nanomaterial and for graphical methods, viz., line graph methods using the weighted normalized specifications.

5.4. Illustrative example of selection of nanomaterial

For using this proposed methodology by anyone first time they have to first identify the applications for what purpose they are using this methodology and corresponding pertinent attributes. Also define the requirements of research and product development carefully. Because without identify the applications, identifying the pertinent attributes, defining the requirements he will never eliminate the large list of nanomaterial to a manageable list.

After defining the requirements applied the pertinent attributes requirements and eliminate infeasible nanomaterial (elimination done on the basis of pertinent attributes one by one) from the available 'n' attributes database/knowledge base and prepare a manageable list of nanomaterial as shown in **Table-1.27** and **Table-1.28**.

Let us take an example of selection of a nanomaterial for "**manufacturing of industrial nanodevice"** for which a requirement of nanomaterial will be as follows:-

The minimum requirement for present application is as shown in **Table-1.27**.

Specific surface area	**Minimum110m^2/g**
Young's modulus	within 83-126 GPa
Thermal conductivity	2483W/m/K
Tensile strength	55GPa
Aspect ratio	~1000
Metallic behaviour	it should be metallic in nature
Wear Resistance	Better wear resistance

Table-1.27.Minimum requirements of application

From the database generated, after 'elimination search' it is easily find out manageable number of candidate nanomaterial and their pertinent attributes tabulated in **Table-1.28.**

Alternate Nanomaterial	Specific surface area	Young's modulus	Thermal conductivity	Tensile strength	Aspect ratio
	g/cm^3	GPa	W/m-K	GPa	
AgNW115	193	79	2850	12	205
NanoXactTM AU Nanoparticles	212	910	1870	15	71
QGraphene® - 50	160	1020	2520	26	1000
QSI-Nano® Silver	189	411	2730	62	58
AgNW60	280	60	2509	50	70
NanoPore™ HP-150	256	168	1705	34	150
Q Tubes® 250	290	107	3000	55	1000

Table-1.28.Attributes for short listed candidate nanomaterial

Step1. Formation of decision matrix, 'D'

By using **Table-1.28** Prepare a decision matrix. The matrix which will contain all the magnitudes of specifications. In this matrix, rows represent the candidate nanomaterial and the column represents the pertinent attributes.

In this example 7 candidate nanomaterial and 5 attributes are considered with their values are listed below:-

$$D = \begin{bmatrix} 193 & 79 & 2850 & 12 & 205 \\ 212 & 910 & 1870 & 15 & 71 \\ 160 & 1020 & 2520 & 26 & 1000 \\ 189 & 411 & 2730 & 62 & 58 \\ 280 & 60 & 2509 & 50 & 70 \\ 256 & 168 & 1705 & 34 & 150 \\ 290 & 107 & 3000 & 55 & 1000 \end{bmatrix}$$

..... (13)

Attributes for the short listed candidate nanomaterial listed in **Table-1.28.**

Step 2.Construction of relative importance matrix A.

After identify the applications from different applications as per the requirement, the relative importance of different attributes for different application is different.

Now for selected application we define this as $a_{ij} = w_i/w_{j,\ where}$ this ratio represents the relative importance of i^{th} attribute with respect to the j^{th} attribute corresponding to the particular

application. Mostly this will be obtain by team of experts by preparing the questionnaires and send it to other team of experts of same area and prepare a database matrix by calculating the average values and put into the relative importance matrix.

A group of experts will determine the relative importance of the attributes with respect to each other.

$$\mathbf{A} = \begin{bmatrix} \mathbf{1} & \mathbf{0.665} & \mathbf{2} & \mathbf{0.665} & \mathbf{3} \\ \mathbf{0.665} & \mathbf{1} & \mathbf{0.665} & \mathbf{2} & \mathbf{2} \\ \mathbf{0.335} & \mathbf{0.5} & \mathbf{1} & \mathbf{0.5} & \mathbf{2} \\ \mathbf{0.5} & \mathbf{0.335} & \mathbf{0.5} & \mathbf{1} & \mathbf{0.5} \\ \mathbf{3} & \mathbf{0.335} & \mathbf{0.335} & \mathbf{0.665} & \mathbf{1} \end{bmatrix} \quad \ldots\ldots\ldots\ldots \quad (14)$$

Step 3 Finding out the maximum Eigen value of the relative importance matrix A.

Eigen value formulation provides to find out the weight vector as shown below:-

$$(A - \lambda I)\, W = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (19)$$

Where, I is the identity matrix, and W is the weight vector.

This equation can also be written as

$(A - \lambda\, I) = 0$ and $W = 0$, Where this gives a trivial solution having no meaning.

$$\mathbf{(A- \lambda\, I)} = \begin{bmatrix} \mathbf{1-\lambda} & \mathbf{0.665} & \mathbf{2} & \mathbf{0.665} & \mathbf{3} \\ \mathbf{0.665} & \mathbf{1-\lambda} & \mathbf{0.665} & \mathbf{2} & \mathbf{2} \\ \mathbf{0.335} & \mathbf{0.5} & \mathbf{1-\lambda} & \mathbf{0.5} & \mathbf{2} \\ \mathbf{0.5} & \mathbf{0.335} & \mathbf{0.5} & \mathbf{1-\lambda} & \mathbf{0.5} \\ \mathbf{3} & \mathbf{0.335} & \mathbf{0.335} & \mathbf{0.665} & \mathbf{1-\lambda} \end{bmatrix} \quad \ldots\ldots\ldots\ldots \quad (15)$$

$(A- \lambda\, I) \;\; = 0$

$\lambda = 8, -0.4038 \pm 0.4910i, -0.4762 \pm 0.5246i$

After solving the characteristics polynomial equation, by using the power method λ_{max} is calculated. From this, λ =8 is the maximum value, as by taking the largest λ value the correct equation is obtained.

Therefore, λ_{max} = 8. Now put this value in Equation (16)

$$(A-\lambda_{max} I) = \begin{bmatrix} -7 & 0.665 & 2 & 0.665 & 3 \\ 0.665 & -7 & 0.665 & 2 & 2 \\ 0.335 & 0.5 & -7 & 0.5 & 2 \\ 0.5 & 0.335 & 0.5 & -7 & 0.5 \\ 3 & 0.335 & 0.335 & 0.665 & -7 \end{bmatrix}$$

..... (16)

Step 4 Calculating weights for each attribute using the Eigen vector associated with maximum Eigen value.

$$(A-\lambda_{Max} I)\, W = 0 \qquad \text{..... (17)}$$

$$\begin{bmatrix} -7 & 0.665 & 2 & 0.665 & 3 \\ 0.665 & -7 & 0.665 & 2 & 2 \\ 0.335 & 0.5 & -7 & 0.5 & 2 \\ 0.5 & 0.335 & 0.5 & -7 & 0.5 \\ 3 & 0.335 & 0.335 & 0.665 & -7 \end{bmatrix} \begin{bmatrix} w1 \\ w2 \\ w3 \\ w4 \\ w5 \end{bmatrix}$$

..... (18)

$$w_1 + w_2 + w_3 + w_4 + w_5 = 1 \qquad \text{..... (19)}$$

W1= 0.3975, W2 = 0.2885, W3 = 0.0590, W4 = 0.1813, W5 = 0.0737

Step 5 calculating the normalized specification matrix using Esq.-(1)

$$r_{ij} = d_{ij} \Big/ \left(\sum_{i=1}^{m} d_{ij}^2 \right)^{1/2} \qquad \text{..... (20)}$$

The normalization helps to provide the dimensionless elements of the matrix.

$$\mathbf{N} = \begin{bmatrix} 0.3166 & 0.0546 & 0.4314 & 0.1115 & 0.1422 \\ 0.3477 & 0.6210 & 0.2831 & 0.1394 & 0.0492 \\ 0.2624 & 0.7060 & 0.3815 & 0.2417 & 0.6937 \\ 0.3100 & 0.2845 & 0.4133 & 0.5764 & 0.0402 \\ 0.4593 & 0.0415 & 0.3798 & 0.4648 & 0.0485 \\ 0.4110 & 0.1162 & 0.2581 & 0.3160 & 0.1040 \\ 0.4757 & 0.0740 & 0.4542 & 0.5113 & 0.6937 \end{bmatrix} \quad \text{.....} \quad (21)$$

Step 6. Calculating the weighted normalized specification matrix using Esq.-(5).

Here incorporate the relative importance of the attributes with their normalized value to create unique parameter for the candidate nanomaterial

$$\mathbf{V} = \begin{bmatrix} 0.1258 & 0.0157 & 0.0254 & 0.0202 & 0.0104 \\ 0.1382 & 0.1791 & 0.0167 & 0.0252 & 0.0036 \\ 0.1043 & 0.2036 & 0.0225 & 0.0438 & 0.0511 \\ 0.1232 & 0.0820 & 0.0243 & 0.1045 & 0.0029 \\ 0.1825 & 0.0119 & 0.0224 & 0.0842 & 0.0035 \\ 0.1633 & 0.0335 & 0.0152 & 0.0572 & 0.0076 \\ 0.1890 & 0.0213 & 0.0267 & 0.0926 & 0.0511 \end{bmatrix} \quad \text{.....} \quad (22)$$

The weighted normalized specification matrix is all-inclusive matrix, which takes care of the attribute values and their relative importance. So the matrix will be able to provide good basis for comparison with each other and with the benchmark nanomaterial.

TOPSIS method based ranking

The weighted normalized attributes for the +ve and _ve benchmark nanomaterial be obtained as

The weighted normalized attributes for the +ve benchmark nanomaterial is calculated by taking the largest value from all the columns with respect to all the pertinent attributes in correspondence to their candidate nanomaterial.

Theoretically best solution of nanomaterial

V* = (0.1890, 0.2036, 0.0267, 0.1045, and 0.0511) ..... (23)

Similarly, The weighted normalized attributes for the -ve benchmark nanomaterial is calculated by taking the smallest value from all the columns with respect to all the pertinent attributes in correspondence to their candidate nanomaterial.

Theoretically worst solution of nanomaterials

v^- = (0.1043, 0.0119, 0.0152, 0.0202, and 0.0029) ..... (24)

Values of Separation from the +ve benchmark nanomaterials **S*** and Values of Separation from the -ve benchmark nanomaterials $\mathbf{S}^-$ is given below.

$S^*_1 = 0.2193$	$s^-_1 = 0.0252$
$S^*_2 = 0.1087$	$s^-_2 = 0.1706$
$S^*_3 = 0.1042$	$s^-_3 = 0.1992$
$S^*_4 = 0.1464$	$s^-_4 = 0.1116$
$S^*_5 = 0.1987$	$s^-_5 = 0.1438$
$S^*_6 = 0.1840$	$s^-_6 = 0.0730$
$S^*_7 = 0.5777$	$s^-_7 = 0.1223$

Relative closeness to ideal solution

$C^*_1 = 0.1030$, $C^*_2 = 0.6108$, $C^*_3 = 0.6565$, $C^*_4 = 0.4325$, $C^*_5 = 0.4198$, $C^*_6 = 0.2840$, $C^*_7 = 0.1747$

Graphical method based Ranking

The element values of weighted normalized specification matrix are used for the line graph plotting. Subsequently, COS can be calculated from graphs. The calculated COS is tabulated as follows.
Suppose the area under the line graph for weighted normalized specifications of first candidate nanomaterial and for benchmark nanomaterial are $AV_1^L = 0.1294$; $AV_{+B}^L = 0.4548$. The coefficient of similarity based on the weighted normalized specification of the first candidate nanomaterial is

$COS_1^{VL} = AV_1^L / AV_{+B}^L = 0.2845$ ..... (25)

Similarly closeness of the candidate nanomaterial with the +ve benchmark nanomaterial obtained from TOPSIS and the graphical methods are tabulated as shown in **Table 12** Thus the nanomaterial are ranked in order of preference based on the attributes selected. For the purchase of a new nanomaterial, the management can use the above ranking effectively to select the nanomaterial, which will be best suitable for the application and is based on this set together with other considerations.

Evaluation and ranking of the candidate nanomaterial using TOPSIS methods as shown in **Table-1.29.**

Candidate Nanomaterials	TOPSIS-Closeness to the +ve benchmark nanomaterial C*	Rank based on C*	COS based on Line Graph COS^{VL}	Rank Based on COS^{VL}
AgNW115 (N1)	0.1030	7	0.2845	7
NanoXactTMAU Nanoparticle (N2)	0.6108	2	0.6418	2
QGraphene® - 50 (N3)	0.6565	1	0.7642	1
QSI-Nano® Silver (N4)	0.4325	3	0.6020	3
AgNW60 (N5)	0.4198	4	0.4650	5
NanoPore™ HP-150 (N6)	0.2840	5	0.4206	6
Q Tubes® 250 (N7)	0.1747	6	0.5729	4

Table-1.29.Evaluation and ranking of the candidate nanomaterial

5.5. Role of user in selection

Here one see, the ranking done by TOPSIS and graphical methods vary from each other. Even for both graphical methods the ranking is not same. The user find out which method is the best suited for his application. Thus the nanomaterial are ranked in order of preference based on the attributes are selected. However, before a final decision is taken to purchase a new nanomaterial, the following factors come into picture: (1) Economic considerations, (2) Availability, (3) Management constraints, corporate policies, (4) International market policies, which were not previously considered in coding and evaluation. Even if the above consideration, say, economic considerations, does not allow the user to buy the top ranked nanomaterial, the user knows which one to go for as the next choice. For example, 2nd and 3rd ranked nanomaterial costing the same, but as our result indicates, the 2nd ranked nanomaterial will perform better in other aspects even though their price is same.

5.6. Results and Discussion

Here, illustrative problem of ranking and selection of nanomaterial is solved using TOPSIS method and graphical method. The problem considering seven candidate nanomaterial and five attributes as shown in **Table-1.28.** This problem is solved using TOPSIS methodology,

which is described in Section 5.3 and according to step V of proposed method, normalized value of material selection attributes for nanomaterial are calculated by using Equation (20).In this example, specific surface area of nanomaterial is non-beneficial attributes and the remaining 4 attributes are beneficial attributes. The normalized data of the material selection attributes are shown in Normalized specification matrix as Equation (21).

Results: By applying the 3-stage procedure for optimum selection and ranking of nanomaterial as discussed in section 4 of proposed methodology, results are obtained. The results for the selection and ranking of nanomaterial are obtained via, TOPSIS method and Graphical methods and it is compared with each other for selection of nanomaterial for given application as given in **Table-1.29**.The evaluation and ranking of the nanomaterial using the novel graphical methods done by their similarity to +ve benchmark nanomaterial. As Coefficient of similarity (COS) is the ratio of area under the curve or enclosed by the polygon for the candidate to that of the benchmark nanomaterial. The value of COS be any +ve fraction ($0 \leq COS \leq 1$) and a measure of the closeness of candidate nanomaterial with the benchmark nanomaterial. The candidates with COS magnitude closer to unity are preferable, since it indicates the closeness to the +ve benchmark nanomaterial.

Discussion: Here, TOPSIS method is used and had considered attributes weight according to an importance and capability of nanomaterial as W_j = [3, 1, 4, 3, 2, 5]. Here, we obtained the ranking an order of ideal solution is N3 > N2 > N4 > N5 > N6> N7> N1, whereas graphical method suggests the ranking an order of ideal solution is N3 > N2 > N4 > N7 > N5> N6> N1. It is recommend that nanomaterial alternative N3, i.e. QGraphene® - 50 is the first choice, and NanoXactTM AU Nanoparticle, QSI-Nano® Silver, AgNW60, NanoPore™ HP-150, Q Tubes® 250 and AgNW115 are placed in the second, third, fourth, fifth, sixth and seventh choices, respectively. Whereas, Graphical method suggests nanomaterial alternative N3, i.e. QGraphene® - 50 the first choice, NanoXactTM AU Nanoparticle, QSI-Nano® Silver are second and third choice, Q Tubes® 250, AgNW60 placed in fourth and fifth choice and NanoPore™ HP-150 and AgNW115 placed in sixth and seventh place respectively. Both the methods suggest that material alternative N1, i.e. AgNW115 is the last choice. According to the TOPSIS method QGraphene® - 50 is the best alternative because of high thermal conductivity, young's modulus and aspect ratio this alternative is selected as most appropriate for the considered application.

5.7. Concluding Remarks

Nanomaterial selection procedure based on the Multiple Attribute Decision Making (MADM) approach, which is a concept used not so frequently for the purpose. It identifies the various attributes needing to be considered for the optimum evaluation and selection of nanomaterial. It provides a coding system for nanomaterial depicting the various attributes. It recognizes the need for, and processes the information about, relative importance of attributes for a given application without which inter-attribute comparison is not possible. It presents the result of the information processing in terms of a merit value, which is used to rank the nanomaterial in the order of their suitability for the given application. The method is especially suitable for generating data of nanomaterial available in the market and their subsequent retrieval. It provides coding scheme to produce electronic database of globally available nanomaterial. he data will be helpful to all sorts of people related to nanomaterial from manufacturer, designers, and users to maintenance personnel. It will be helpful to improve the overall productivity of the organization.

CHAPTER-6

CONCURRENT DESIGN OF NANOACTUATOR

FOR

X-ABILITIES

"MADM Approach"

In this chapter, main concern about the organizations that are deploying well designed nanoactuators supporting converged applications of defense, mechanical industry and biological applications etc. Use of different applications demands nanoactuator to have various abilities – actuation , modification, realization, performance etc, called x- abilities- in varying degree of importance depending on application requirements of an organization. To facilitate design of nanoactuator simultaneously for all x – abilities in an integrated way, a concurrent design methodology using multiple attribute decision making (MADM) approach is proposed in this chapter. This concurrent design methodology is aimed at including design time considerably and makes use of expertises of experts from different specialized fields in a single design team. MADM approach provides technique for selection of best nanoactuator for the application under consideration. Here, in this chapter attempts are made to propose a concurrent design methodology for design of a nanoactuator for x-abilities using MADM approach. This design for x-abilities enables the designers to focus on various abilities at conceptual design stage on one hand and concurrent design approach helps reduce design time considerably. TOPSIS technique using MADM approach ensures that the chosen alternative is as close to ideal solution as possible, and as far from the negative-ideal solution as possible.

6.1. Introduction

Ever growing demand of nanoactuators for high productivity includes use of various model arrangements for variety of applications designing a nanoactuator that supports converged applications require careful considerations of type of applications that the nanoactuator needs to support and the types of actuators resources theses applications require. There are a number of issues that must be considered for the nanoactuator design; some are common to all applications. Designing nanoactuator for actuation, modification, realization and performance one at a time is not time consuming but also requires various iterations as design requirements/constraints for ability considered at later stage may require revisiting design for ability already considered . Many of the research contributions have been published in the field of actuation, design, performance, positioning and realization of nanoactuator. Most of these studies focus each ability of a nanoactuator at a time. On the other hand almost all the studies published in the area of design for x-abilities and concurrent design are in the field of manufacturing, construction etc. Relatively no one has contributed in the design of nanoactuator using concurrent engineering for x-abilities, at the same time no literature is available for selection of nanoactuator elements using multi attribute decision making (MADM) approach. For the past decade nanotechnology has greatly influenced all science and engineering branches including physics electronics, civil engineering material engineering etc. In the electronic world, nano-electromechanical systems (NEMS) have

become the center of interest for developing ultra-small devices. There are several kinds of NEMS actuated by electrostatic forces including flexural actuators as well as torsional actuators. The physical behavior of the torsional actuators has been extensively studied in micro scales . Many researchers contributed in the field of manufacturing and construction sector of nanodevices including nanoactuator by considering various models and physical characteristics/attributes/properties depending on various applications.

6.2. Design Flow/Methodology

A combined approach of concurrent engineering design and design for x-abilities is proposed. Concurrent engineering design methodology enables faster design cycle by using principles of concurrent engineering via, simultaneous consideration of design constraints, combing experts from different fields into a design team, etc. Design for x-abilities is system approach that simultaneously considers all the design goals (abilities) constraints.

6.2.1. Design for x-abilities

The design for x-abilities refers to considering simultaneously all product or application specific design goals (abilities) and constraints at the beginning of the design. Various products/services require many of the abilities in varying degree of importance to suit application specific needs. For example to design/build an optimum nanoactuator understanding of inherent attributes. Properties, strengths and weaknesses of nanoactuator infrastructure/architecture are required. A nanoactuator may need to satisfy certain performance requirements for a set of applications to work efficiently in addition to be able to recover from damage/failure, to ensure proper step and actuation. This requires the nanoactuator to have the x-abilities via, actuation, modelisation, realization and performance.

6.2.2. Concurrent Engineering Design

Concurrent engineering is a systematic approach to integrate the concurrent design of products/services and processes used to design, manufacturer and support the product/service. In this approach, the design team considers all elements of the product life cycle from conception through disposal including quality, cost, schedule, and user requirements. For example, concurrent design of nanoactuator includes design of a nanoactuator for all the required abilities via, actuation, modelisation, realization, performance etc.

6.2.3. MADM Technique

MADM techniques are product selection techniques. Multiple attributes are processed in MADM techniques for ranking finite number of alternatives to arrive at a single choice for the best product. For this we uses a Technique for Order Preferences by Similarity to Ideal Solution (TOPSIS) MADM technique to select a best possible nanoactuator element. The specifications of nanoactuator elements are considered as attributes for arriving at best possible nanoactuator element to deploy in the nanoactuator having required ability.

6.3. Concurrent Design of Nanoactuator for x-abilities

6.3.1. Design Flow

Figure-2.4 shows the design flow of the proposed design methodology. The design of nanoactuator starts with specifying objective and considering application requirements of users. Experts or team of experts from different field work simultaneously to design Nanoactuator possessing respective ability via, actuation, modelisation, realization, performance. Four parallel paths represent this, each for an x-ability in design flow. Each different team intends to identify pertinent attributes concurrently for each x-ability considering technological and infrastructure standards, specifications, features, and constraints. Three overlapping steps of collecting design information, technological and infrastructure consideration shows this. The design teams then use these pertinent attributes to select specification of technology and nanoactuator elements with their relative importance. As shown by two overlapping steps of selecting specifications and assigning relative importance. All the specifications selected by different teams individually for each x-ability are united maintaining their relative importance. Ranking and selection of nanoactuator elements is then done using TOPSIS method – a MADM approach.

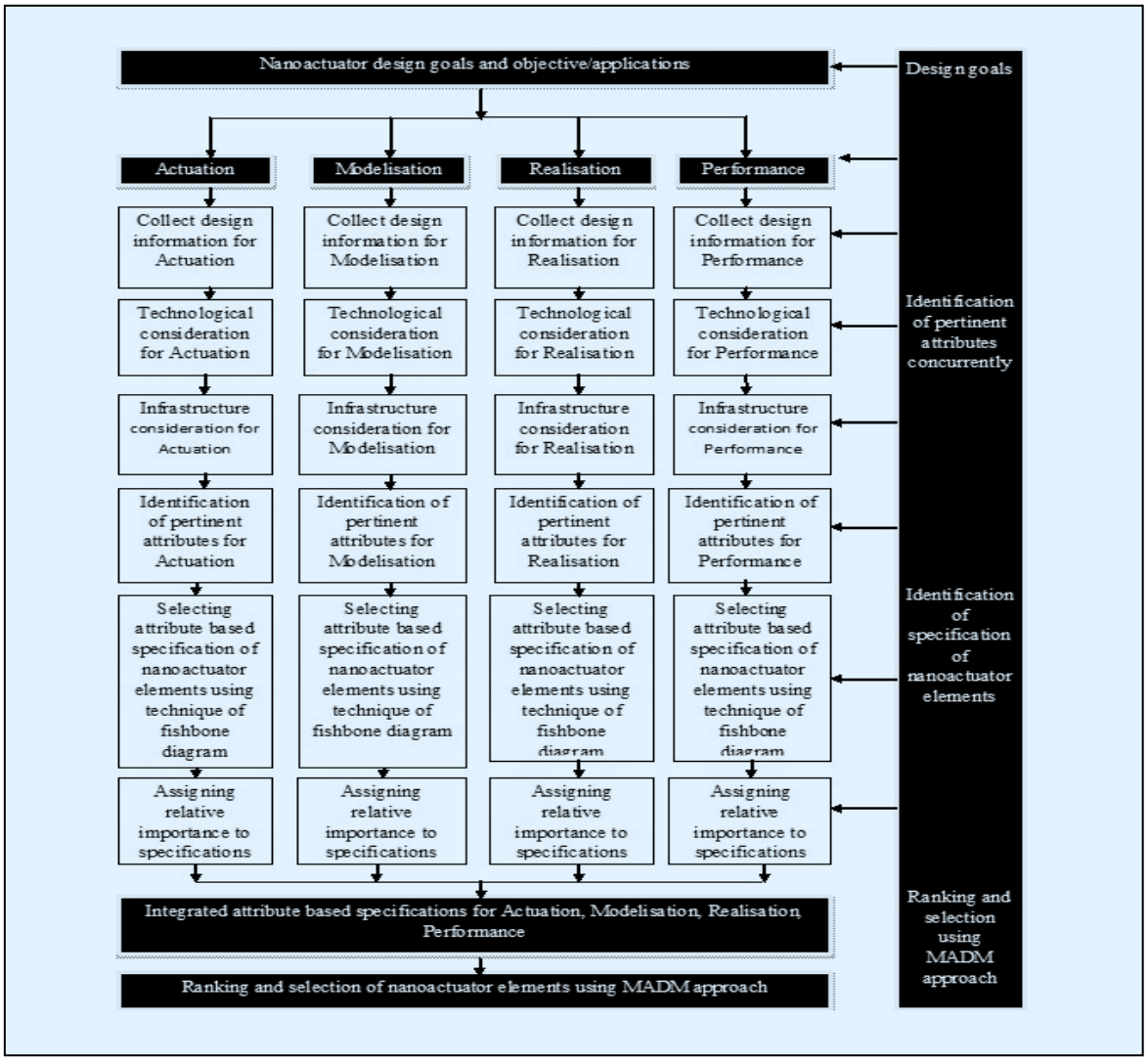

Figure-2.4.Design flow for concurrent design of nanoactuator for x-abilities

6.3.2. Design Goals

Design goals of the nanoactuator define the purpose of design of nanoactuator. The predetermined performance criteria or abilities required for applications are considered For example, if the application demands a guaranteed stick slip effect for leg displacement of the slider, then nanoactuator design will need to take this into consideration and may place actuation as high priority. Following are some of the common abilities that almost all nanoactuator posses with varying degree of importance based on application.

6.3.2.1. Actuation

The actuation plays an important role in design of nanoactuator. Like, mechanism of thermal actuation has been widely investigated and implemented to build MEMS actuators **[152].** In this, one of the key design goals of a nanoactuator is the reversibility of mechanochemical actuation the ability to produce nanostructures by utilizing the already well developed micro fabrication technology is of advantage for the production process as well as for the integration of NEMS, MEMS, and ICs in constructing a fully functional device. The combination of thermal actuation principle and the insĭtu fabrication nanotechnology for a thermally driven nanoactuator is also used. Due to the small dimension of these nanowires, the actuation process can only be carried out and observed in a Scanning Electron Microscope (SEM) initial actuation also affects the deflection of the nanoactuator. In biological field, the actuation mechanism depends on the modification of electrostatic charges along the peptide by varying the pH of the solution resulting in the reversible movement of helices and, therefore, creating the motion of an actuator The actuation mechanism depends on the creation of similar electrostatic charges along the peptide chain which forces the two coils to repel each other and move apart thus creating an opening tweezers-like motion of the nanoactuator.. In the field of nanodevices, interestingly for long/thin enough nano-beams, electrostatic actuation can cause the movable component to deflect and rotate simultaneously. Hence, actuation requirements need to be considered at initial stage of deciding nanoactuator objective and application requirements.

6.3.2.2. Modelisation

Modelisation refers to consider various aspects while designing any nanodeveices, such aa accurately model, simulate and analyze very complex electromagnetic, electromechanical, and vibroacoustic phenomena in motion nanodevices in order to optimize the design, e.g., increase efficiency, maximize the torque density, attenuate vibrations and noise, etc. performing modeling, simulation and analysis, the designer optimizes nanomachine performance. Maxwell's equations are used to attain high-fidelity modeling **[151].** Integrated with the relationships for electromagnetic torque, torsional-mechanical dynamics and virboacoustic transient behavior must be used to model synchronous reluctance nanoactuators in the full operating envelope. The main challenge associated with computational modeling of bionanosystems is the size of the system that can be efficiently simulated. Nemirovsky **[162]** were the first researchers to introduce a lumped-mass model to capture the torsion/bending coupled behavior of torsional micro-actuators. The size dependent behavior of the constitutive material is modeled using non-classical augmented continuum theory.Alos, mechanical, inertia and piezoelectric model is most widely used. Modelisation is one of the key ability to be considered initially while designing a nanoactuator.

6.3.2.3. Realization

Few realizations have been proposed for the ten past years, with different forms and goals. Zesch **[175]** proposed a one-degree-of-freedom (DOF) impact drive NanoStep, actuated by two masses connected with a piezoelectric stack actuator and using a unique V-groove guiding rail. He also proposed a NanoCrab, which is a rotational micro motor based on the stick–slip principle, using three shear piezoelectric elements. Baumann **[179]** proposed a 3-DOF micro robot, based on stick–slip drive, that can position loads up to 1 g in a spherical workspace of 6 cm in diameter with a resolution of about 100 nm: Breguet and Clavel **[180]** developed a 1-DOF stick–slip actuator that reaches relatively high speeds (typically 5 mm=s) with a 1:5 mm range. A permanent magnet is used to allow it to work upside down. No guiding system has been foreseen for this robot. Moreover, the price of such equipment is not compatible with the realization of a simple and cheap positioning system. The effects of size reduction on the performances of the actuator are currently studied in the department, aiming to get higher resonance frequency, which would offer the opportunity to work at higher frequencies, allowing high-speed translation and, in the case of a working frequency higher than 20 kHz; silent working. Another field to Explore is the guiding system.

6.3.2.4. Performance

The performance refers to the parameters, constraints and various techniques and methods in order to enhance the performance of any nanodevice. Generally, performance of the nano-actuator such as maximum speed, resolution, open loop accuracy, maximum driving force and rigidity are measured with laser interferometer. Another point of interest is the lifetime of actuator: as they can usually perform billions ð109Þ of cycles without loss of performance, leading to a working time between 28 and 280 h with working frequencies between 10 and 1 kHz: because of surface irregularities, the performances are not optimal and the accumulation of small losses during a longer time interval leads to a smaller mean velocity. The effects of size reduction on the performances of the actuator are currently studied aiming to get higher resonance frequency, which would offer the opportunity to work at higher frequencies, allowing high-speed translation. Perform coherent electromagnetic, mechanical, and thermodynamic design with performance analysis synergetic assessing synthesis, design and optimization. Nanoactuators performance depends upon nanomachine operating principle, topology, materials, etc. In case of biological field, molecular dynamics simulations were performed on VPL peptides in order to study the performance of the nanoactuator. The length of the VPL peptides, the role of the solvent (and solvent composition), binding energies to various target objects, are other variables that need to be investigated in order to assess conditions for optimum performance, (I. e. for example maximum force and stability, a given velocity etc.) TMD and Steered Molecular Dynamics (SMD)] can be used to study the performance of the nanoactuator while bound to a platform. Mother Nature has her own set of molecular machines that have been working for millennia, and have been optimized for performance and design over the ages. Analytical lumped-mass models to simulate the pull-in performance of torsional micro mirrors. Herein, the size dependent pull-in performance of torsional nano-actuator is investigated considering both coupling and size effects for the first time.

6.3.3. Design, Technological, and Infrastructure Consideration

After establishing design goals, the next step is to form design teams that will identify relevant attributes for a particular x-abilities. Separate teams are formed for each x-ability

that will work concurrently to reduce design cycle time. Each team then intends to collect design information required to identify relevant attributes considering application requirements. For example, a design team works on performance ability is required to consider attributes like cycle ratio, repeatability for step displacement. Similarly, a design team working on actuation is required to consider the relevant attributes like stick slip effect for the travel range of the step, resolution for the amplification, legs and system displacement to allow for expansion of future requirements. In the next stage, various technological and infrastructure issues are to be taken into account. For example, which model is to be used for modeling the nanoactuator, fabrication of a nanoactuator structure using MWNT as a bimorph layer, but not as a. Template, in order to create the device in a much simpler way, and (2) direct force measurement from nanoactuators, which is not yet reported. To create nanoscale bimorph structures, the key fabrication issue is the deposition of a metal film on only one side of a MWNT exposing the other side as a bare MWNT surface, requiring a directional deposition method. How should the nanoactuator elements are well recognized, how should it be managed, what will be the future requirements, what is the development schedule, etc, are the important issues for consideration by the design team.

6.3.3.1. Identification of Pertinent Attributes for X-Abilities

A list of some of the common attributes for particular abilities is shown below. All the attributes many not be relevant for all the applications. There may be some of the attributes that are relevant **[181]** not included in the list.

Actuation Attributes

Following are some of the key attributes, which can be considered while designing a nanoactuator for actuation:-

- Travel
- Accumulation
- Force
- Amplification

Modelisation Attributes

Important attributes of nanoactuator design for modelisation could be:-

- Mechanical Aspect
- Thermal Aspect
- Electrical Aspect
- System Displacement

Realization Attributes

Realization of the nanoactuator can be achieved by doing different fuctions as an attributes are listed below:-

- Motion Transmission
- Control Parameters
- Guiding Aspects

Performance Attributes

Performance attributes are those that are required to be maintained in order to enhance the performance of nanoactuator are listed below:-

- Topology
- Power Balance
- Positioning system
- Driving Aspect

6.3.3.2. Identification of Specification of Nanoactuator Elements

6.3.3.2.1. Selection of Attribute Based Specification of Nanoactuator Elements

In the next step, the design teams intend to select and assign relative importance to specifications of nanoactuator elements- , via, Slider, Casing, Motor stages, Benders, Sensors, Capacitor, Resistor, Legs, Guiding grooves, Material, Rack, Electrode plates and Magnet etc- that are put in use to achieve the design goals. . For this each specifications of each nanoactuator element- e.g. Travel range, resonant frequency, Resolution, Static large signal stiffness, etc of motor stage – is considered one at a time for each pertinent attribute identified. Each specification, which contributes add value to attributes and in turn to an x-ability, is identified. Relative importance is assigned to each specification based on the number of relevant attributes, it adds value or influences for all x-abilities taken together. The selection of specifications of nanoactuator elements and their relative importance is achieved using fishbone diagram as shown in **Figure-2.5-2.8**.

The fishbone diagram, also referred to as root-cause analysis, provides a systematic way of looking at effects and causes that create or contribute to those effects. Through fishbone diagram found applications mainly in analyzing a problem/issue to determine root cause, it can be used to identify specifications that contribute to a feature/ability during design of product/service.

As can be seen from **Figure-2.5**, all the attributes which add value to Actuation of nanoactuator identified in the section ‘Actuation Attributes’ are represented by major bones of the fishbone diagram. For example, Depends on various design criteria in mind simple and inexpensive system with macroscopic travel range and high resolution is used. For this either accumulation or an amplification system is used. The latter one could not produce an infinite travel; therefore because of surface irregularities, Accumulation which can be achieved by the nanoactuator is directly proportional to the step size and multiple equilibrium positions. The performances are not optimananl and the accumulation of small losses during a longer time interval leads to a smaller mean velocity, so for that accumulation has been chosen.

For build a simple system, eliminate the accumulation principles that are more complex to design walking, hopping which is hard to control and rolling which needs a large amount of parts and is difficult to miniaturize., sub-bones in the fishbone diagram of **Figure-2.5** show this. In this way, relevant features/specifications for the entire nanoactuator elements are identified, which contribute add value to each attributes are represented in a fishbone diagram of **Figure-2.5**. Similarly, a fishbone diagram for each x-ability is prepared. **Figure-2.6-2.8** represents fishbone diagrams for modelisation, realization and performance of nanoactuator.

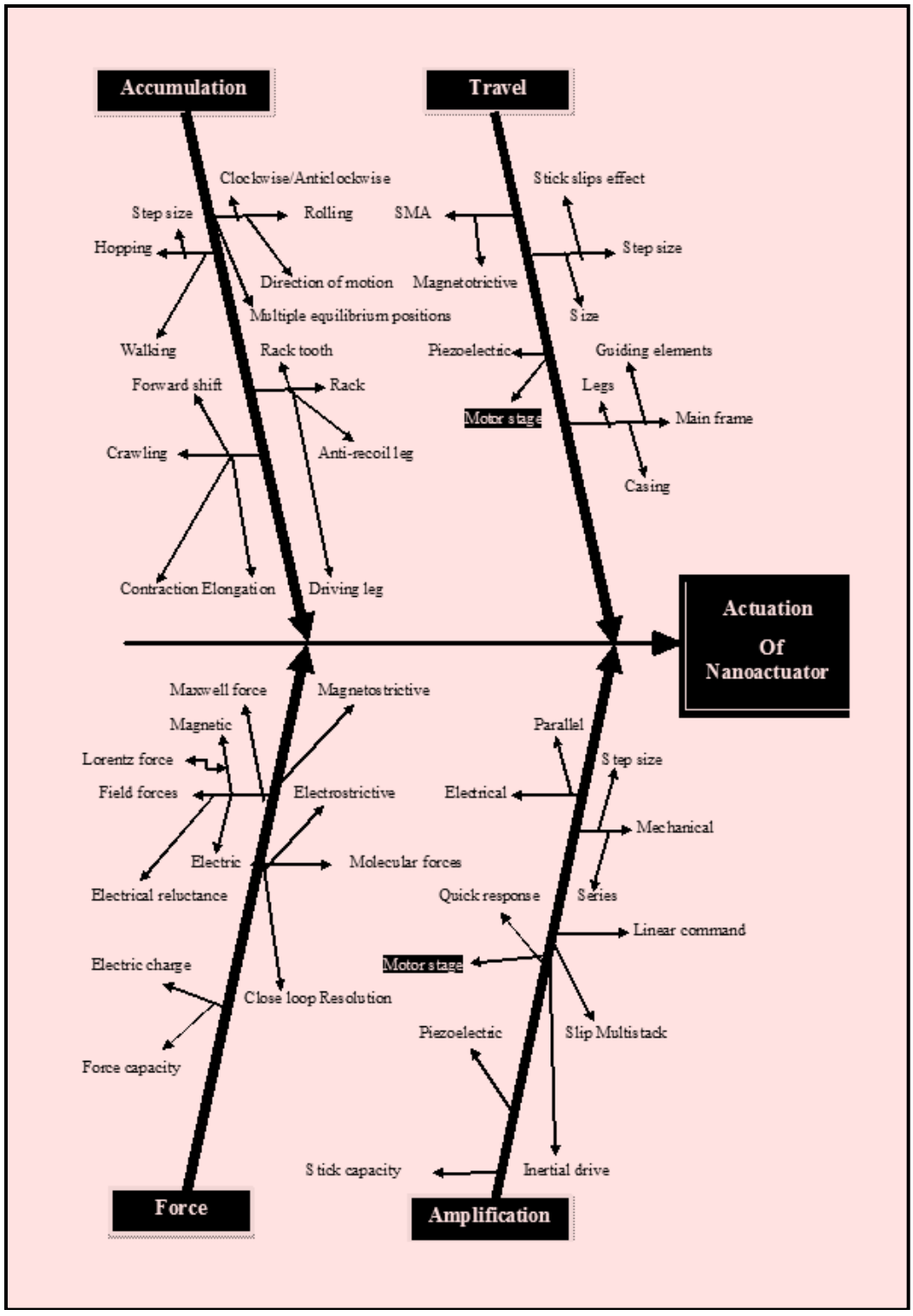

Figure-2.5.Fishbone diagram Actuation

All the attributes identified in the section 'Modelisation Attributes' under different aspects and factors – e.g. system displacement, Mechanical aspect etc – that adds value to modelisation of nanoactuator are represented by major bones of fishbone diagram of **Figure-2.6**

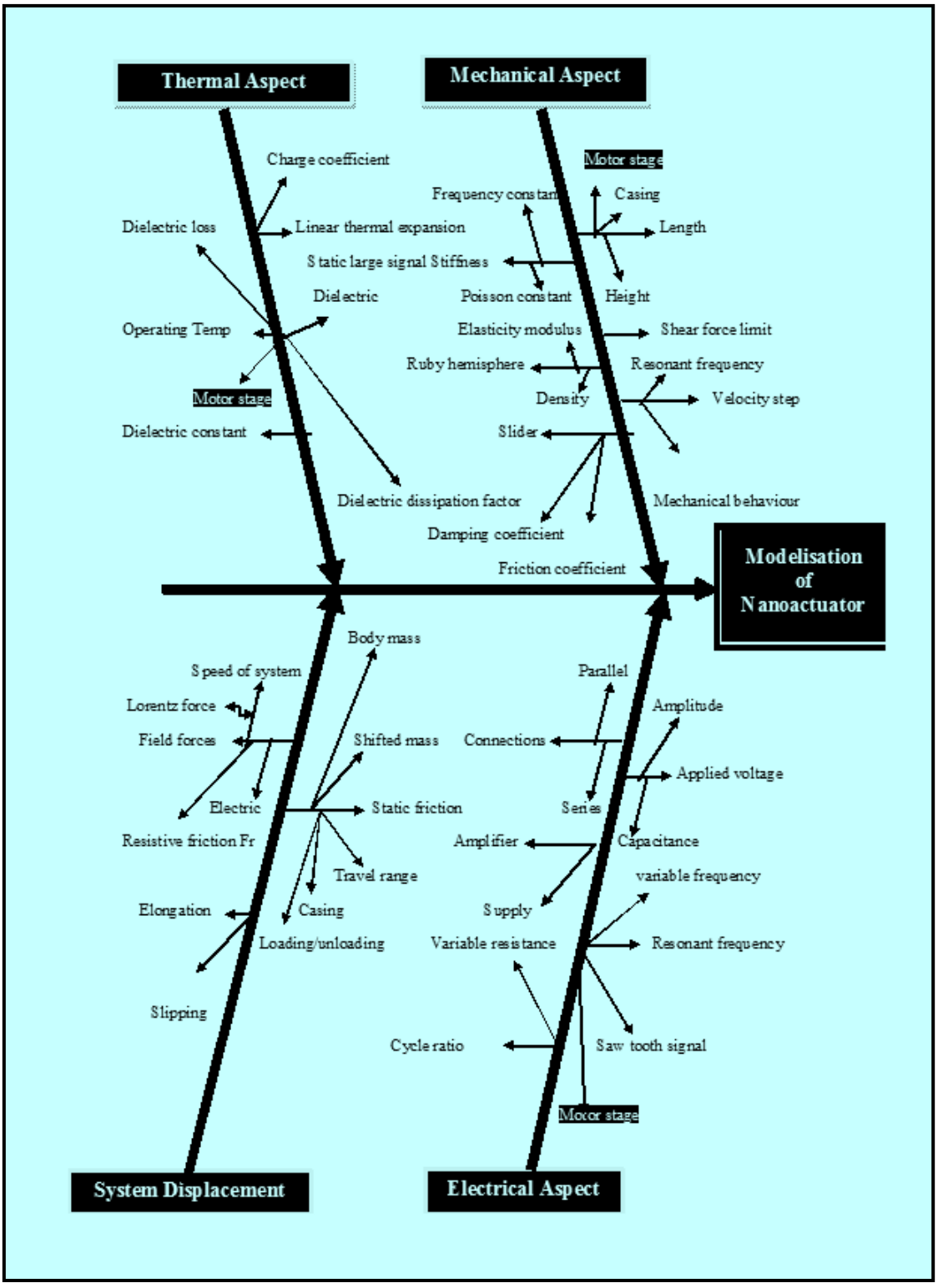

Figure-2.6.Fishbone diagram Modelisation

Thus in order to control the system displacement and in turn, better modelisation of nanoactuator, nanoactuator elements with better values of those specifications are preferred, which give rise to achieve better and controllable system displacement. System displacement is mainly depends on the Speed of the system, which in turn gives rise to better modelisation

of nanoactuator, can be achieved with better values of travel range and resistive friction force etc and other nanoactuator elements.

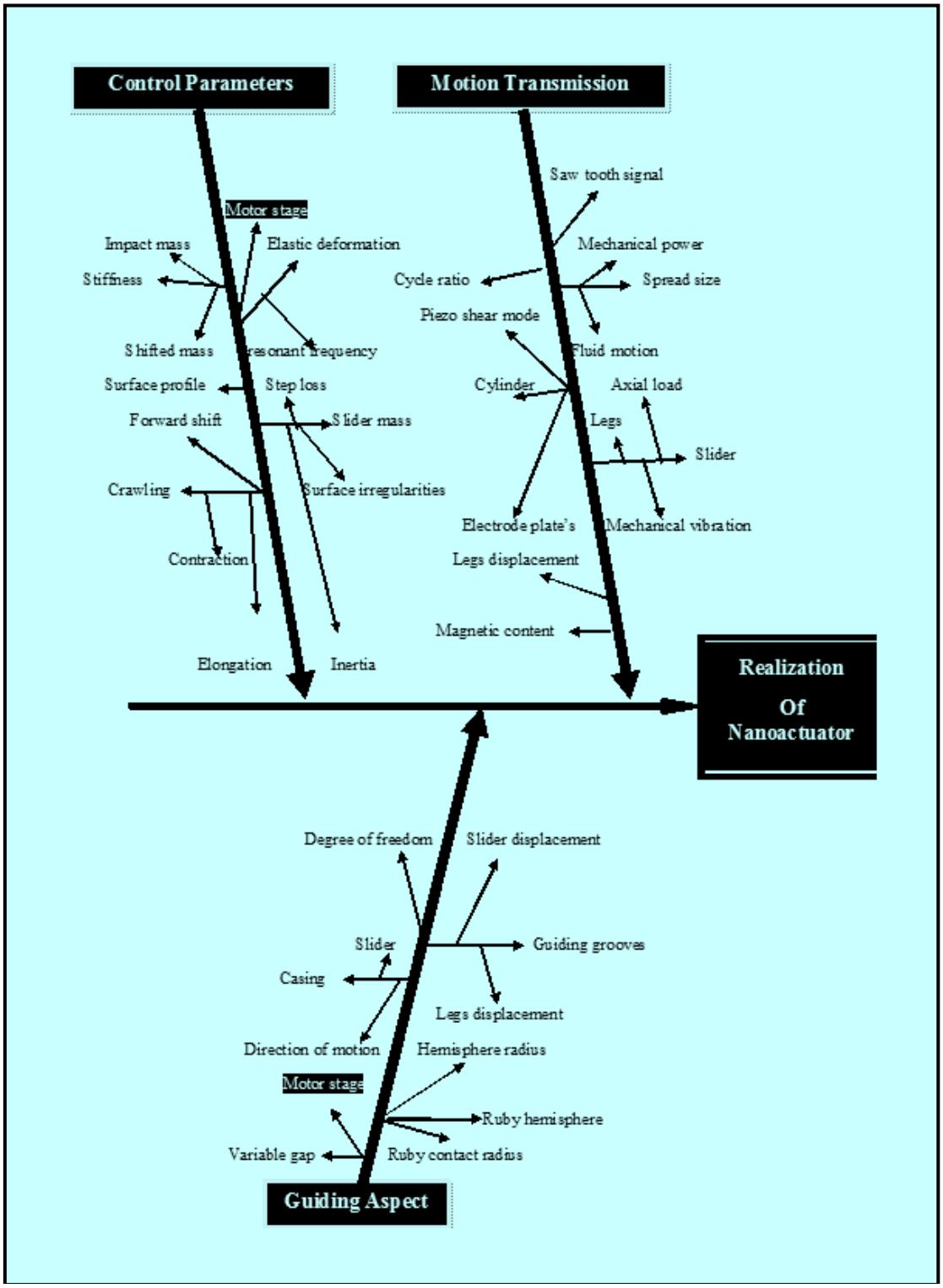

Figure-2.7.Fishbone diagram Realization

Likewise, sub-bones and sub-sub-bones for mechanical aspect, thermal aspect and electrical aspect indicates specifications of nanoactuator elements that cause better valuation of sub-

attributes that in turn causes better valuation for attributes and finally modelisation of nanoactuator. In this way, relevant features/specifications for the entire nanoactuator elements are identified, which contribute to add value to each attribute as represented in a fishbone diagram of **Figure-2.6**.

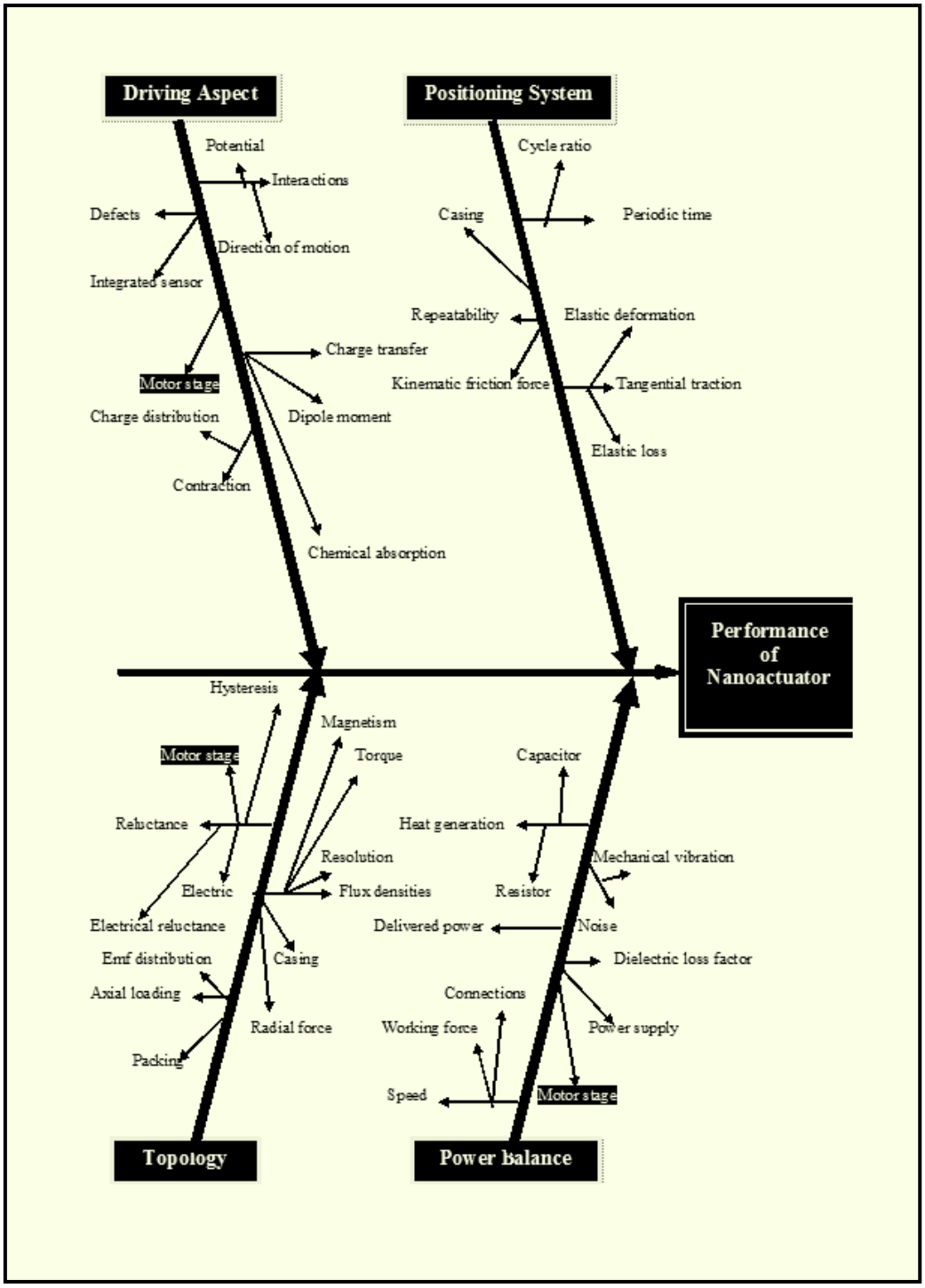

Figure-2.8.Fishbone diagram Performance

Likewise, major bones of fishbone diagram of **Figure-2.7**. Represents all the attributes which adds value to realization of nanoactuator identified in section 'Realization Attributes'

which are Control parameters, Motion transmission and Guiding aspects. In order to have better motion transmission between the legs and in turn, better realization of nanoactuator, higher values of those specifications of nanoactuator elements are preferred, which contribute to achieve better motion transmission. Sub-bones in the fishbone diagram of **Figure-2.7** exhibit that motion transmission becomes smooth by controlling the motion of legs displacement, fluid flowing through the nanoactuators and mechanical vibration of the slider between the legs. Sub-sub-bones of **Figure-2.7** finally identify that the better values of specification of magnetic content, mechanical power and axial load, which in turn improves motion transmission giving rise to better realization of the nanoactuator. In the same way, performance of nanoactuator can be improved by taking intoConsideration all the different aspects like, Topology, Power balance, driving aspect and positioning system. Major bones of the fishbone diagram in **Figure-2.8** show this, Sub-bones in **Figure-2.8** further denotes basic foundation to achieve better values of these attributes. For example, most important part for driving aspects of nanoactuator is the integrated sensor, charge transfer and various interactions that have been used in order to drive the nanoactuator as per the appropriate working conditions.

6.3.3.2.2. Assigning Relative Importance to these Specifications

Experts in the field assign the relative importance to these specifications using various yardsticks. One such yardstick can be the number of relevant features it adds value or influences a specification in a fishbone diagram of **Figure-2.5** for actuation, it can be seen that close loop travel influences four relevant attributes. These are Travel range, Accumulation, Force and Amplification. Step size influences three relevant attributes – via Actuation, Amplification and Travel Range – Push/pull force capacity influences the only relevant attribute of amplification. Hence, relative importance of these specifications can be approximated to 5, 5, 4, 4, 1, and 1 respectively, for closed loop resolution, step size, closed loop travel range, stick slip effect, Push/pull force capacity, and direction of motion. Similarly, fishbone diagram of **Figure-2.6** gives relative importance of specifications of motor stage for modelisation. The specifications static large signal stiffness influence the one attribute- via mechanical aspect- and shear force limit influences three of the attributes – via, thermal aspect, electrical aspect and system displacement. Hence, relative importance of specifications can be 5, 5, 4, 3, 3 and 1, for static large signal stiffness, shear force limit, friction coefficient, ruby hemisphere, Dynamic operating current coefficient and behavior, respectively. **Figure-2.7** gives relative importance of stiffness and resonant frequency for motor stage for realization, which is 5 and 5, respectively. Similarly, **Figure-2.8** gives relative importance of Travel Range, Shear force limit, static large signal stiffness, resonant frequency and closed loop resolution for performance, which is 1, 2, 3, and 5, respectively. Assigning relative importance is to be repeated for other nanoactuator elements via- Slider, Motor, Benders, Sensors, Capacitor, and Resistor, Legs, Guiding grooves, Material, Rack, Electrode plates and Magnet etc for each x-ability. The entire process i.e. identification, selection of attributes based specifications of nanoactuator elements and assigning relative importance to these specifications is to be done concurrently by separate team for each x-ability so as to reduce design time.

6.3.3.3. Combining Results

Close loop resolution	**3.6 nm**
Static large signal stiffness	150 N/µ m
Pull/push force capacity	3 N
Stick slip effect	Maximum
Direction of motion	Along the step displacement
Shear force limit	147µN
Friction coefficient	0.5
Ruby hemisphere	With hemisphere radius 0.26nm
Dynamic operating current coefficient	85µA
Behaviour	Mechanical
Resonant frequency	2.8 kHz
Close loop travel range	5.7.1.

Table-1.30.Combined relative importance of specification of motor stage

6.3.3.3.1. Combination of Attribute Based Specification for X-Abilities

Assigning Relative Importance to Combined Specification as shown in Table-1.30

Now the result of above four concurrent design steps for each x-ability is to be united to achieve overall goal of design for x-ability. By considering each x-ability to be quality important average relative importance of each specification can be taken as combined relative importance for specifications of x-abilities. The weight age is subjected to the other factors under consideration Thus to design for x-abilities combined relative importance of specification of motor stage is as follows:

6.3.3.3.2. Short Listing of Alternatives

Short- listed alternatives may be obtained from different design teams/experts or as suggested by vendors.

For example, following motor stages may be considered for an application under consideration the specifications stick slip effect, direction of motion, friction coefficient, shear force limit, friction coefficient, ruby hemisphere and dynamic operating current coefficient are supported by all the short listed motor stages and hence these may be omitted during ranking and selection of motor stages. As shown in **Table-1.30**.

Alternative motor Stages	Close loop Travel µm	Push/Pull force N	Close loop resolution nm	Static large signal stiffness N/µm	Resonant frequency kHz
M-661.4P0	20	3	0.1	2	208
M-662.4P0	19.5	2	0.2	3	198
M-663.4PR	20	3	0.3	5	268
M-664.164	25	4	0.1	3	212
M-665.2PM	50	5	0.1	4	274
M-674.264	50	7	0.05	5	155

Table-1.31.Short- listed alternatives for motor stage

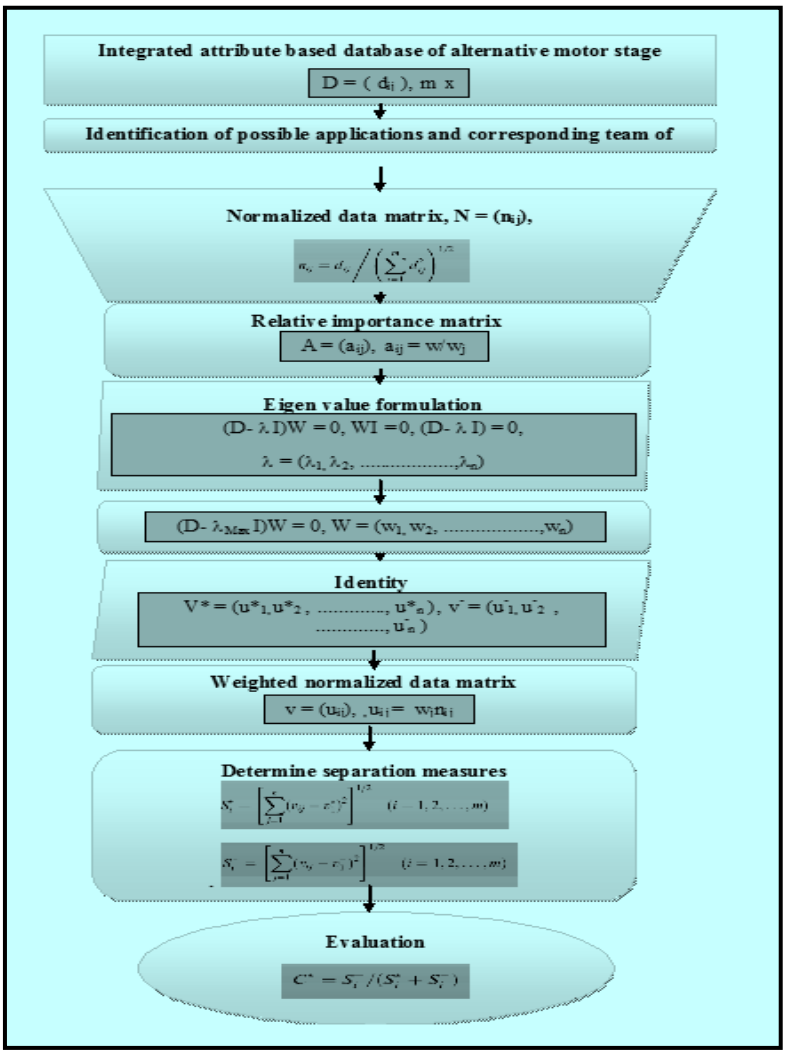

Figure-2.9.shows a flowchart of the TOPSIS technique

6.3.3.4. Ranking and Selection using MADM

Now, the selection of nanoactuator elements can be done using MADM approach (TOPSIS technique) As shown above. MADM methods choose or rank finite number of alternatives that are measured by few relevant attributes. TOPSIS is the techniques used to rank these alternatives. The steps involved are shown in **Figure-2.9** with example of selection of motor stage as follows

6.3.3.4.1. Representation of Alternatives as Decision Matrix

Decision matrix, 'D' is a 'm x n' matrix where each row represents 'm' number of short-listed alternatives- motor stage attributes in our example- and column represents 'n' number of specifications via travel range and static large signal stiffness. For close loop resolution of the motor stage lowest value is preferred hence inverse of resolution is to be considered for computation.

$$D = \begin{bmatrix} 20 & 3 & 10 & 2 & 208 \\ 19.5 & 2 & 5 & 3 & 198 \\ 20 & 3 & 3.3 & 5 & 268 \\ 25 & 4 & 10 & 3 & 212 \\ 50 & 5 & 10 & 4 & 274 \\ 50 & 7 & 20 & 5 & 155 \end{bmatrix} \quad \text{..... (1)}$$

6.3.3.4.2. Arriving at Normalized Specification Matrix

Normalized specification matrix, N, provides dimensionless quantities and is calculated using normalization of the decision matrix, D, by using

$$n_{ij} = d_{ij} \Big/ \left(\sum_{i=1}^{m} d_{ij}^2 \right)^{1/2} \quad \text{..... (2)}$$

Column wise normalization,

Where d_{ij} is an element of the decision matrix, D, Thus,

$$N = \begin{bmatrix} 0.2424 & 0.2834 & 0.3686 & 0.2132 & 0.3808 \\ 0.2363 & 0.1889 & 0.1843 & 0.3198 & 0.3625 \\ 0.2424 & 0.2834 & 0.1216 & 0.533 & 0.4906 \\ 0.303 & 0.3779 & 0.3686 & 0.3198 & 0.3881 \\ 0.6061 & 0.4724 & 0.3686 & 0.4264 & 0.5016 \\ 0.6061 & 0.6614 & 0.7372 & 0.533 & 0.2837 \end{bmatrix}$$

..... (3)

6.3.3.4.3. Computation of Relative Importance Matrix

Relative importance matrix, A, is formed by storing pair-wise comparisons of relative importance of specification obtained in previous section. This is an 'm x n' matrix, where a_{ij} contain the relative importance of ith specification over the jth specification.

$$A = \begin{bmatrix} 1 & 0.665 & 2 & 0.665 & 3 \\ 0.665 & 1 & 0.665 & 2 & 2 \\ 0.335 & 0.5 & 1 & 0.5 & 2 \\ 0.5 & 0.335 & 0.5 & 1 & 0.5 \\ 3 & 0.335 & 0.335 & 0.665 & 1 \end{bmatrix}$$

..... (4)

6.3.3.4.4. Calculation of Relative Weights of the Specifications

In the next step, relative weights of the specification can be obtained by the Eigen vector method using following steps.
Take Eigen values of relative importance matrix A, x_{max} corresponding to the largest Eigen value λ_{max}, as all the elements of x_{max} are either positive or negative **[202].**
Find the sum of the elements of x_{max} as

$$\alpha = \sum_{i=1}^{n} (x_i)_{max}$$

..... (5)

Find weight vector w as

$$w = (x_{max})/\alpha \text{ such that } \sum_{i=1} w_i = 1. \quad \text{..... (6)}$$

$$w_1 + w_2 + w_3 + w_4 + w_5 = 1 \quad \text{..... (7)}$$

Performing these three steps gives relative weights:-

W_1= 0.3975, W_2 = 0.2885, W_3 = 0.0590, W_4 = 0.1813, W_5 = 0.0737

6.3.3.4.5. Weight Assignment

Assigning these weights to normalized specifications matrix gives weighted normalized specification matrix, 'v

$$V = \begin{bmatrix} w_1 n_{1,1} & w_2 n_{1,2} & \cdots & w_n n_{1,n} \\ w_1 n_{2,1} & \ddots & \cdots & \vdots \\ \vdots & \vdots & \ddots & \vdots \\ w_1 n_{m,1} & w_2 n_{m,2} & \cdots & w_n n_{m,n} \end{bmatrix} = \begin{bmatrix} v_{1,1} & v_{1,2} & \cdots & v_{1,n} \\ v_{2,1} & \ddots & \cdots & \vdots \\ \vdots & \vdots & \ddots & \vdots \\ v_{m,1} & v_{m,2} & \cdots & v_{m,n} \end{bmatrix} \quad \text{..... (8)}$$

Therefore,

$$V = \begin{bmatrix} 0.0963 & 0.0817 & 0.0217 & 0.0386 & 0.282 \\ 0.0939 & 0.0544 & 0.0108 & 0.0579 & 0.0267 \\ 0.0963 & 0.0817 & 0.0071 & 0.0966 & 0.0361 \\ 0.1204 & 0.109 & 0.0217 & 0.0579 & 0.0286 \\ 0.2409 & 0.1362 & 0.0217 & 0.0773 & 0.0369 \\ 0.2409 & 0.1908 & 0.0434 & 0.0966 & 0.0209 \end{bmatrix} \quad \text{..... (9)}$$

6.3.3.4.6. Ranking and Selection by TOPSIS

Ranking and selection of nanoactuator elements, motor stage, is done using TOPSIS method.

The separation from the positive benchmark nanoactuator element, Si*, is

$$S_i^* = \left[\sum_{j=1}^{n}(v_{ij} - v_1^*)^2\right]^{1/2} \qquad (i = 1, 2, \ldots, m)$$

..... (10)

From the negative benchmark nanoactuator element, S_i^-, is,

$$S_i^- = \left[\sum_{j=1}^{n}(v_{ij} - v_1^-)^2\right]^{1/2} \qquad (i = 1, 2, \ldots, m)$$

..... (11)

Then, the relative closeness to the positive benchmark nanoactuator element, C*, is calculating using

$$C^* = S_i^- / (S_i^* + S_i^-)$$

..... (12)

The calculated C* values are, $C^*_1 = 0.1423$, $C^*_2 = 0.0897$, $C^*_3 = 0.2629$, $C^*_4 = 0.3015$, $C^*_5 = 0.6572$, $C^*_6 = 0.9126$,

Ranking of the nanoactuator elements is done in descending values of C* i.e. most preferred nanoactuator element has maximum C* value. A nanoactuator element with largest value of C_6^* is preferable, i.e. M-674.264 motor stage is preferable for x-abilities under consideration.

6.3.3.5. Concluding Remark

This chapter helps in designing an optimum nanoactuator which is important in order to achieve desired functionality. This requires best possible nanoactuator element to put in use considering all the x-abilities. After specifying nanoactuator objectives and considering application requirements of the user, design of nanoactuator starts with identifying pertinent attributes concurrently for each x-ability, via, actuation, modelisation, realisation and performance etc, by different team of experts considering technological and infrastructure standards, specifications, features, and constraints. Design teams then uses these pertinent attributes to select specifications of technology and nanoactuator elements with their relative importance using fishbone diagram. All the specifications selected by different teams individually for each x-ability are integrated maintaining their relative importance. TOPSIS technique, MADM approach, is used for selection of best possible nanoactuator elements based on relative importance of specifications of nanoactuator elements. This design for x-abilities enable the industry designers to focus on various abilities at conceptual design stage on one hand and concurrent design approach helps reduce design time and product cycle considerably on the other hand. This methodology finds usefulness in design of various other products/services that has different attributes/features/quality standards/performance requirements. Once the nanoactuator is designed and put in use, the fishbone diagram prepared can assist in sensitivity analysis. Fishbone diagram uses various attributes identified concurrently for each x-ability.

CHAPTER-7

CONCLUSIONS AND FUTURE RECOMMENDATIONS

7.1. Conclusions

In this thesis, **Chapter 3** represents attribute based literature review methodology with knowledge base. In which different attributes are identified on the basis of cause and effect diagram. Proper identification of different attributes and their quantification, coding has been done in a very efficient and reliable manner. Methodology helps the different researchers, designer, manufacturer and industrialist by providing them those attributes which are benefited for their respective field of work. Identification of different research papers and sorting of those papers based on application, process, techniques etc in which more or less work is done are easily calculated. Methodology provide a computer based information Matrix software with the help of which relative importance of any attributes with respect to any paper can be easily determined. Different issues are addressed in a very effective manner with the help of information Matrix. Information Matrix is a permanent source of knowledge and need to be updated so that everyone takes more benefit from database. Methodology is proposed only for nanomaterial, but it can also extended by the recommendation of the author in all the areas of nanotechnology.

In this thesis, **Chapter 4** represents a system methodology for developing a nanotechnology system by considering all the attributes responsible for fabrication, design and process parameters along with the interactions between the constituents is proposed using a digraph and matrix approach. It is a powerful tool for modelling the degree to which nanotechnology constituents interact with each other. It shows how these interactions affect the process parameters, design, and production attributes. The present work identifies five characteristics, which parameterize the nanotechnology system.

i. The system methodology consists of the nanotechnology system digraph, the nanotechnology system matrix, and the nanotechnology permanent function. The nanotechnology digraph is a mathematical representation of the structural characteristics and their interdependence, useful for visual modelling and analysis. The nanotechnology system matrix converts digraph into another mathematical form. The nanotechnology system permanent function is a mathematical model characterizing the structure of the nanotechnology system and also helps one to determine nanotechnology system index. Different terms of the permanent function lead to a set of analysis tests for strength, weakness, opportunities, threats and optimization of nanotechnology.
ii. This multi-attribute (structural constituents) characterization of nanotechnology system into a single numerical index. If multivariable P_is and P_{ij}s are represented by numerical values in the variable adjacency matrix. Thus, the numerical index of a nanotechnology system derived from a multinomial is used for comparison, rating, and optimum selection.
iii. The present work emphasizes the numerical methodology of nanotechnology system that can also optimize the design and the production parameters. A generalised methodology is also proposed to model a system consisting of N subsystems and their interactions. This study gives a criterion how to compare two nanotechnology systems with the help of permanent function on structure basis.

Chapter 5 presents a nanomaterial selection procedure which helps in selecting the appropriate nanomaterial based on the modelling of nanotechnology system using Multiple Attribute Decision Making (MADM) approach, which is a concept used not so frequently for the purpose. It identifies the various attributes needing to be considered for the optimum evaluation and selection of nanomaterial. It provides a coding system for nanomaterial depicting the various attributes. It recognizes the need for, and processes the information about, relative importance of attributes for a given application without which inter-attribute comparison is not possible. It presents the result of the information processing in terms of a merit value, which is used to rank the nanomaterial in the order of their suitability for the given application. The contributions of the work be summarized as

1. The method is especially suitable for generating data of nanomaterial available in the market and their subsequent retrieval. It provides coding scheme to produce electronic database of globally available nanomaterial.
2. The data will be helpful to all sorts of people related to nanomaterial from manufacturer, designers, and users to maintenance personnel. It will be helpful to improve the overall productivity of the organization.
3. Here by identifying 168 attributes of the nanomaterial, the attempt has been made to codify most of the nanomaterial characteristics, which will define the nanomaterial precisely and accurately. The coding scheme is illustrated with example.
4. Evaluation and ranking based on the mathematical and graphical approaches along with the illustrative examples are given.

In **Chapter 6**, after selecting the appropriate nanomaterial required for designing an optimum nanoactuator in order to achieve desired functionality is done. This requires best possible nanoactuator element to put in use considering all the x-abilities.

i. After specifying nanoactuator objectives and considering application requirements of the user, design of nanoactuator starts with identifying pertinent attributes concurrently for each x-ability, via, actuation, modelisation, realization and performance etc, by different team of experts considering technological and infrastructure standards, specifications, features, and constraints.
ii. Design teams then uses these pertinent attributes to select specifications of technology and nanoactuator elements with their relative importance using fishbone diagram. All the specifications selected by different teams individually for each x-ability are integrated maintaining their relative importance.
iii. TOPSIS technique, MADM approach, is used for selection of best possible nanoactuator elements based on relative importance of specifications of nanoactuator elements. This design for x-abilities enable the industry designers to focus on various abilities at conceptual design stage on one hand and concurrent design approach helps reduce design time and product cycle considerably on the other hand.
iv. This methodology finds usefulness in design of various other products/services that has different attributes/features/quality standards/performance requirements. Comparison of existing design procedures with the proposed one is made. Once the nanoactuator is designed and put in use, the fishbone diagram prepared can assist in sensitivity analysis. Fishbone diagram uses various attributes identified concurrently for each x-ability. These design steps consider all the relevant x-abilities of nanoactuator from the initial design phase itself that helps reduce design time considerably. Thus a concurrent design methodology for design of nanoactuator for x-abilities using MADM approach is accomplished

7.2. Future Recommendations

i. The derivation and importance of the numerical index of a nanotechnology system will be given in future work with illustrative examples.

ii. An attempt will be made in future publications to correlate nanotechnology performance characteristics with the nanotechnology structural model reported in this thesis.

iii. The application of MCDM with improved version of 'TOPSIS' "A target based normalization techniques for nanomaterial selection will be given in future work with illustrative examples.

iv. Eigen vector method as used in conventional TOPSIS method used for evaluation, comparison, ranking and optimum selection of MEMS products, processes, software components, designs etc.

v. Improved version of TOPSIS "A target-based normalization technique for nanomaterial selection, Modified TOPSIS, Fuzzy and Extension of TOPSIS will be used on the same problem discussed in this thesis sections, comparison of results and discussion will be presented in future publications.

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