

# CHAPTER I

## INTRODUCTION

When one or more dimensions of the solids are reduced sufficiently its physio chemical characteristics depart notably from those of the bulk solid through which reduction in size, novel electrical, mechanical, chemical, magnetic and optical properties can be probed. The resulting structure is then called a low dimensional structure (or system). The confinement of particles, usually electrons or holes to a low dimensional structure leads to a dramatic change in their behavior. Low dimensional structures show new properties in a new way that is different from simply the miniaturization of a particular device. Although the minimum size needed to obtain new properties will vary with many material dependent factors, the value usually falls in the range of a few nanometers. For this reasons, low dimension structures are popularly called nanostructures.

### 1.1 Nanotechnology

“The principles of physics, as far as I can see, do not speak against the possibility of maneuvering things atom by atom. It is not an attempt to violate any laws; it is something, in principle, that can be done; but in practice, it has not been done because we are too big.” The above words, by Richard Feynman in his talk entitled, “there’s plenty of room at the bottom”, during a presentation in a meeting of the American Physical Society in 1959 at Caltech, is widely accepted as the spark that has initiated the present ‘nano’ age (C.P. Poole et.al. 2003). Inspired by Feynman's concepts, K. Eric Drexler independently used the term "nanotechnology" 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 with atomic control. Nanotechnology is thus defined as possessing the following features;

- Nanotechnology involves research and technology development at the 1 nm to 100 nm range.
- Nanotechnology creates and uses structures that have novel properties because of their small size.
- Nanotechnology builds on the ability to control or manipulate at the atomic scale.

## **1.2 Nanomaterials**

Nanomaterials are materials having size in the scale range of approximately 1-100 nm. The prefix “nano” which is derived from the Greek word for dwarf, is referred to the length scale of one billionth of a metre ( $10^{-9}$ ) (E.L. Wolf, 2004). As the grain sizes become so small; a significant volume fraction of the atoms resides in grain boundaries and the materials possess a large number of interfaces (D. Vogel 1995, T. P. Chou et.al, 2007 & S. Rani et.al.2008).

In nanoparticles, the various material properties such as electrical, mechanical, optical, magnetic etc. can be selectively controlled by engineering the size, morphology and composition of the particles (Y. Chenglin et.al, 2007). It is possible to produce nanostructure materials, using a variety of synthesis methods, in the various forms like thin films, powder, quantum wires, quantum wells, quantum dots, etc. Generation of carbon nanostructures, which are related to the famous Bucky ball, is also of considerable interest. Conventional materials have grains varying in size anywhere from hundreds of microns ( $\mu\text{m}$ ) to millimetres (mm). A nanocrystalline material has grains on the order of 1-100 nm. The average size of the atom is of the order of 1 to 2 Å in radius. One nanometre comprises of 10 Å and hence in one nanometre (nm), there may be 3-5 atoms, depending on the atomic radii (S. J. Chang et.al, 2009).

The most intuitive ‘nano-size’ effect is produced due to the dominance of surface atoms in the nanomaterials. If a chunk of a crystal is broken into two, its exposed surface area would increase, thereby slightly increasing the ratio of strained surface bonds to the bulk bonds. If the crystal is kept breaking up into smaller units a situation will come when the surface bonds will dominate over the bulk bonds. The new properties of the material are now determined by strained bonds of the surface atoms (B. Gilbert et.al, 2004). A lower melting point for nanomaterials is one of the several manifestations of the effect of dominance of the strained surface bonds (P. Buffat et.al, 1976).

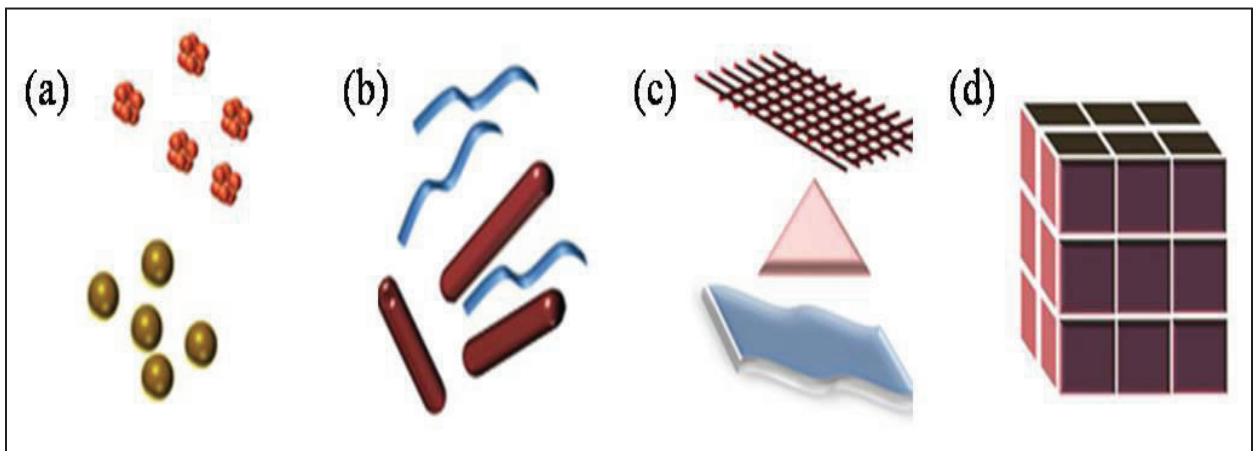
The change in the quantum mechanical states of the electrons in a nanomaterial is another distinct nano-scale effect. There are distinct energy states for single atoms that the electrons can occupy. When lot of atoms come together to form bulk lattice, due to interatomic interactions several closely placed energy states are now available for an excited electron to form a continuum called conduction band. The corresponding ground states merge to form the valence band. However for very small (nano scale) crystals due lack of enough atoms, the availability of energy states for electrons become discrete and far apart. Such nanocrystals are characterized as atomic clusters and are called quantum confined systems (L. Brus, 1986).

### **1.3 Classification of Nanomaterials**

Nanomaterials can be nanoscale in one dimension (eg. surface films), two dimensions (eg. strands or fibres), or three dimensions (eg. particles). They can exist in single, fused, aggregated or agglomerated forms with spherical, tubular, and irregular shapes. Common types of nanomaterials include nanotubes, dendrimers, quantum dots and fullerenes. Nanomaterials have applications in the field of nano technology, and displays different physical chemical characteristics from normal chemicals (i.e., silver nano, carbon nanotube, fullerene,

photocatalyst, carbon nano, silica). According to Siegel, Nanostructured materials are classified as follows:

- Zero dimensional nanostructures - spheres and clusters
- One dimensional nanostructures – nanofibres, nanowires and nanorods
- Two dimensional nanostructures - nanofilms, nanoplates, and networks
- Three dimensional nanostructures – nanomaterials



**Fig 1.1 (a) Zero dimensional (b) one dimensional (c) two dimensional (d) three dimensional nanostructures**

#### **1.4 Thin Films**

Thin film technology is the basic of astounding development in solid state electronics. The usefulness of the optical properties of metal films and scientific curiosity about the behavior of two dimensional solids has been responsible for the immense interest in the study science and technology of the thin films. Thin film studies have directly or indirectly advanced in many new areas of research in solid state physics and chemistry which are based on phenomena uniquely characteristic of the thickness, geometry and structure of the film (A.R. West, 2003).

Thin film materials are the key elements of continued technological advances made in the fields of optoelectronic, photonic and magnetic devices. The processing of materials into thin films allows easy integration into various types of devices. The properties of material significantly differ when analyzed in the form of thin films. Most of the functional materials are rather applied in thin film form due to their specific electrical, magnetic, optical properties or wear resistance. Thin film technologies make use of the fact that the properties can particularly be controlled by the thickness parameter (B. K. Kuanr et.al, 2008).

Nano-sculptured thin films are a new class of films deposited on substrates with controlled azimuthal rotation,  $\omega$  and tilt,  $\theta$ , by a method called glancing angle deposition (GLAD). The understanding and modeling of nano-sculptured films deposited on tilted substrates become increasingly important as their applications encompass various disciplines: photonics liquid crystal display technology, magnetic media information storage, organic or inorganic sensors, energy storage technology, among many other tools.

Thin films are thermally stable and reasonably hard, but they are fragile. On the other hand organic materials have moderate thermal stability and are tough, but are soft. For mechanical device stability four material properties of the device components are important: elastic modulus, yield strength, interfacial adhesion and film fracture toughness. Mechanical properties of thin films often differ from those of the bulk materials. This can be partially explained by the nanostructure of thin films and the fact that these films are adhered to a substrate (C. Fischer-Cripps, 2002).

## 1.5 Synthesis of nanoparticles

The methods of synthesizing the nanomaterials are broadly classified into two types:

- (i) Top-down process
- (ii) Bottom-up process

### (i) Top-down process

In this process, the bulk materials are broken into nano sized particle. Semiconductor technology uses this method. It is a process in which etching and deposition techniques are used to sculpt a substrate. In this process, the materials continuously shrink to smaller dimension. Top-down approach is an example of solid-state processing of materials.

### (ii) Bottom-up process

In this process, nanomaterials are produced by building of atom by atom. In this approach, the powder components are formed first and they are packed into the nanostructured material. Thus the individual atom and molecules are used to construct useful nanostructured materials. There are few widely known methods to produce nanomaterials. Using these methods, it is possible to produce nano-size materials in the form of nano - powders, nano - crystals, nano - films, nano - wires, nano - tube, nano - dots, etc.

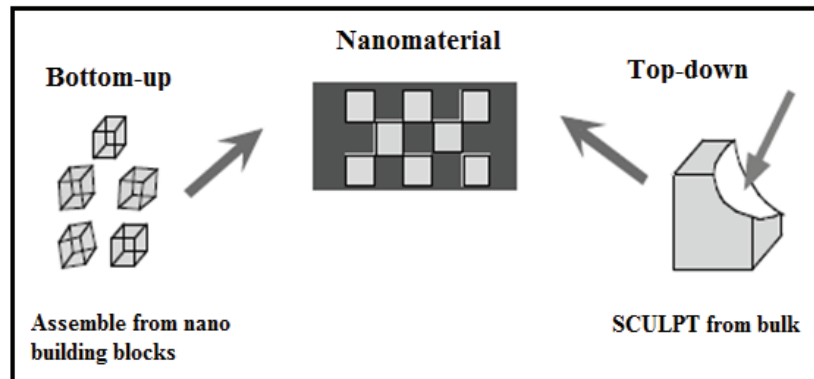


Fig 1.2 Schematic of various approaches for synthesis of nanomaterials

### 1.5.1 Physical Methods

#### *i) Ball milling*

One of the top-down approaches is ball milling method. In ball milling, small hard balls are allowed to rotate inside a container and then it is made to fall on a solid with high force to crush the solid into nano crystal. Ball milling is also known as mechanical alloying or crushing. The hardened steel or tungsten carbide balls are put in a container along with powder of particles ( $< 50 \mu\text{m}$ ) of a desired material. The container is closed with tight lids. When the container is rotating around the central axis, the material is forced to press against the walls. The milling balls impart energy on collision and produce smaller grain size of nano particle. Few milligrams to several kilograms of nanoparticles can be synthesized in a short time. This technique can be operated at large scale.

#### *ii) Plasma arc method*

Plasma is an ionized gas. To produce plasma a potential difference is applied across two electrodes. The gas at low pressure gives up its electrons and gets ionized. Ionized gas (plasma) conducts electricity and an electric arc is maintained between the two electrodes. A typical plasma arcing device consists of two electrodes. When an arc is set up between two electrodes, the material evaporates from anode as positively charged ions. These positive ions are attracted towards the other electrode (cathode) where they pick up the electrons and they are deposited to form nanoparticles.

#### *iii) Vapour phase deposition*

Vapour phase deposition technique is used to fabricate thin films, multilayers, nanotubes, nanofilaments and nanosized particles of different materials. These materials can be organic or inorganic. There are generally two types of vapour phase deposition techniques used in

electronic industry such as, Physical Vapour Deposition (PVD) and Chemical Vapour Deposition (CVD). PVD involves the direct deposition of gaseous phase on the substrate surfaces. CVD on the other hand involves diffusion with chemical reactions at the substrate surfaces. CVD is complex process than PVD.

### **1.5.2 Chemical Methods**

#### *i) Sol-gel method*

This method involves two types of materials or components ‘sol’ and ‘gel’. In solutions, the molecules of nanometer size are dispersed and move around randomly and hence the solutions are clear. In colloids the molecules are suspended in a solvent. When they are mixed with a liquid, colloids look cloudy or even milky. A colloid that is suspended in a liquid is called as sol i.e., sols are solid particles in a liquid. A suspension that keeps its shape is called a gel. Gels are nothing but a continuous network of particles with pores filled with liquid (or polymers containing liquids). Sol-gel method involves formation of ‘sols’ in a liquid and connecting the sol particles (or some sub-units capable of forming a porous network) to form a network. By drying the liquid, it is possible to obtain powders, thin films or even monolithic solid.

In sol - gel formation, first sol can be obtained by the following methods.

- (a) Hydrolysis
- (b) Condensation and polymerization of monomers to form particles
- (c) Agglomeration of particles.

After this, the formation of network which extends throughout the liquid medium is obtained to form a gel. Synthesis of sol - gel in general involves hydrolysis of precursors, condensation followed by polycondensation to form particles, gelation and drying process by various routes. The precursors (starting chemicals) are to be chosen such that they have a tendency to form gels.



The rates of hydrolysis and condensation reactions are governed by various factors such as pH, temperature, molar ratio, nature, concentration of catalyst and process of drying. Under proper conditions spherical nanoparticles are produced.

*ii) Electro-deposition Method*

This technique is used generally in electroplating and in the production of nanofilms. In this technique, two electrodes are immersed inside the electrolyte [aqueous solutions of salt, acids etc]. When the current is passed through the electrodes, certain mass of substance is liberated from one electrode and is deposited on the surface of the other electrode and hence forms a thin nano - film on the surface of the electrode. The thickness of the nano-films can be adjusted by controlling the current and the time of deposition. These films are mechanically robust, highly flat and uniform.

*iii) Wet Chemical Method*

The best method for synthesizing mono dispersed nanoparticles is wet chemical synthesis which is also called as table top method. Wet Chemical synthesis has a further advantage of tunable surface properties of the synthesized nanoparticles, offered by the adsorbed ions (for electrostatic stabilization) or the passivation of polymer. Stable colloidal nanoparticles find many futuristic applications, for example semiconductor and metallic nanoparticles can be used to make futuristic electronic and optoelectronic devices. Wet chemical synthesis method enables the viability for large scale production. Moreover, among the other methods, wet chemical approach is a simple processing and inexpensive technique unlike CVD, PVD and MOCVD methods.

## **1.6 Properties of nanomaterials**

Nanomaterials have the structural features in between of those of atoms and the bulk materials. While most microstructured materials have similar properties to the corresponding bulk materials, the properties of materials with nanometer dimensions are significantly different from those of atoms and bulks materials. This is mainly due to the nanometer size of the materials which render them: (i) large fraction of surface atoms; (ii) high surface energy; (iii) spatial confinement; (iv) reduced imperfections, which do not exist in the corresponding bulk materials. Due to their smaller dimensions, nanomaterials have extremely large surface area to volume ratio, which resulting in more “surface” dependent material properties. This in turn may enhance or modify the properties of the bulk materials.

### **1.6.1 Optical properties**

The optical properties of nanomaterials depend on parameters such as feature size, shape, surface characteristics, and other variables including doping and interaction with the surrounding environment or other nanostructures. Likewise, shape can have dramatic influence on optical properties of metal nanostructures. A simple change in size alters the optical properties of the nanoparticles. However, when anisotropy is introduced to the nanoparticles, such as growth of nanorods, the optical properties of the nanoparticles change dramatically.

### **1.6.2 Electrical Properties**

Electrical Properties of nanoparticles discuss about fundamentals of electrical conductivity in nanotubes and nanorods, carbon nanotubes, photoconductivity of nanorods, electrical conductivity of nanocomposites. One interesting method which can be used to demonstrate the steps in conductance is the mechanical thinning of a nanowire and measurement of the electrical current at a constant applied voltage. The important point here is that, with

decreasing diameter of the wire, the number of electron wave modes contributing to the electrical conductivity is becoming increasingly smaller by well-defined quantized steps.

### **1.6.3 Mechanical Properties**

Mechanical Properties of nanoparticles deals with bulk metallic and ceramic materials, influence of porosity, influence of grain size, super plasticity, filled polymer composites, particle-filled polymers, polymer-based nanocomposites filled with platelets, carbon nanotube-based composites. However, two materials, neither of which is produced by pressing and sintering, have attracted much greater interest as they will undoubtedly achieve industrial importance. Filling of polymers with nanoparticles or nanorods and nanotubes, respectively, leads to significant improvements in their mechanical properties. Such improvements depend heavily on the type of the filler and the way in which the filling is made. Particulate-filled polymer-based nanocomposites exhibit a broad range of failure strengths and strains. This depends on the shape of the filler, particles or platelets, and on the degree of agglomeration. The larger the particles of the filler or agglomerates, the poorer are the properties obtained.

### **1.6.4 Magnetic properties**

The physical and chemical properties of magnetic nanoparticles largely depend on the synthesis method and chemical structure. In most cases, the particles range from 1 to 100 nm in size and may display super paramagnetism.

## **1.7 Semiconductor nanomaterials**

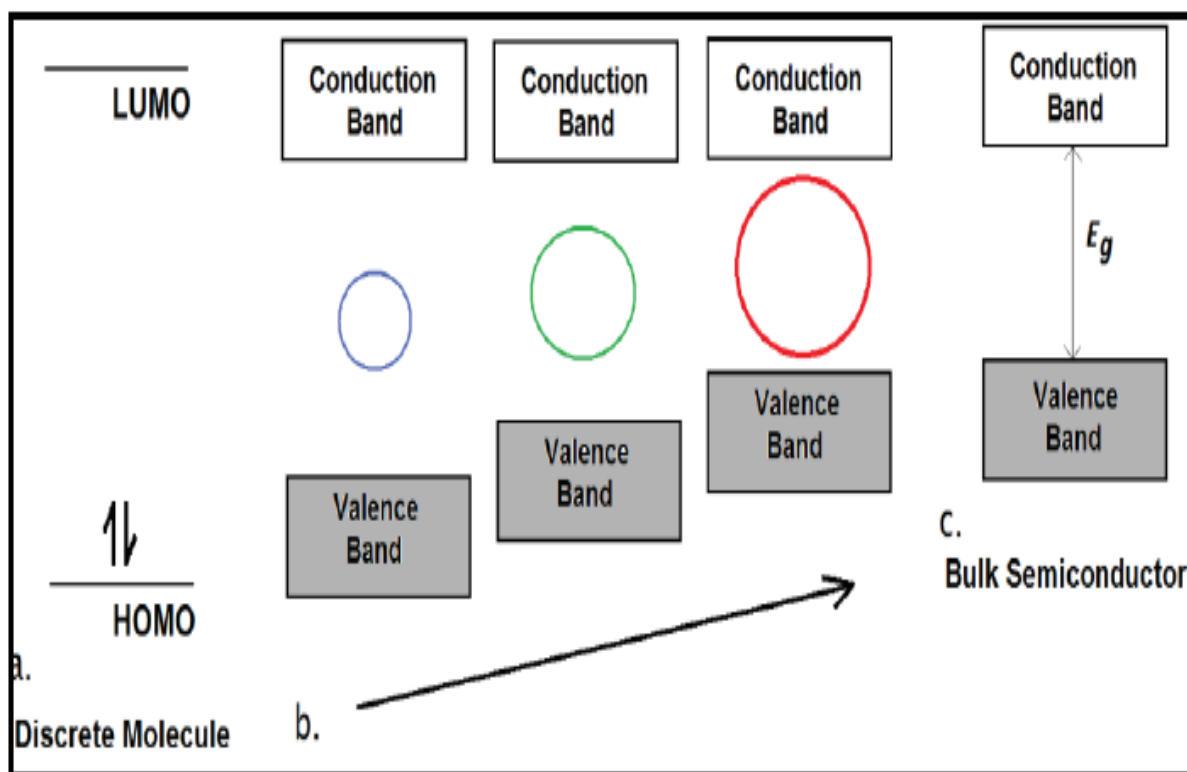
It is usually assumed that the properties of solid semiconductors are independent of their size. However, this assumption is valid for solids containing a macroscopic number of atoms. The electronic excitation of semiconductor crystal results in the formation of a loosely coupled electron-hole pair. In semiconductors, the size of the delocalization area of such a pair can be

many times larger than lattice constant. The decrease in the size of a semiconductor crystal down to a size comparable with the delocalization area of the electron-hole pair, affects the electronic characteristics (R. F. Khairutdinov, 1998). The unusual physico-chemical properties of semiconductor nanoparticles mainly depend on three main factors.

i) The size of nanoparticles is comparable with molecular dimensions. This determines the difference between the kinetics of chemical transformations on the surface and the kinetics of chemical transformations in infinite space.

ii) The surface atoms constitute a considerable proportion of the total number of atoms of a nanoparticle. This affects the thermodynamic characteristics of nanoparticles.

iii) The non-linear optical effects arise and the energies of excitonic transitions in nanoparticles become dependent on the size since it is comparable with the delocalization area of the charge carriers.



**Fig 1.3 Semiconductor nanoparticles with increasing size but smaller than exciton Bohr radius**

### 1.8 Copper Iodide nanoparticles

Copper iodide (CuI), a p-type direct bandgap semiconductor, has attracted the research community for many years because of its wide bandgap, negative spin-orbit splitting and high ionicity, an unusually large temperature dependency, anomalous diamagnetism behavior, large ionicity, new high pressure phase etc.. It has potential applications in superionic conductor, solid-state solar cells, catalysis for synthesis of organic compounds and others (Naoomi Yamada et.al, 2016). Due to the possibility of tuning hole density with iodine doping, high hole mobility ( $43.9 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ) and high transparency in visible region, CuI is a promising candidate to meet out the present need for transparent p-MOS towards the realisation of transparent CMOS technology.

Due to the eco-friendliness of the material, it is used as a source of dietary iodine in table salt and also CuI filled single- and multi-walled CNTs have the potential to be used as biocompatible thermometers (S. Gao et.al 2010, A. Klapars et.al 2002). CuI shows three polymorphic forms namely (i)  $\gamma$ -CuI, in zinc blende structure, exists below 370 °C, (ii)  $\beta$ -CuI, in wurtzite structure, observed between the temperatures 370 to 400 °C and (iii)  $\alpha$ -CuI, in rock salt structure, a high temperature phase which exists above 400 °C (Marius Grundmann et.al 2013, J. B. Boyce et.al 1981). As a p-type transparent semiconductor, CuI is an attractive candidate for transparent solid state lighting devices due to high exciton binding energy of 62 meV and also for transparent thermoelectric devices owing to its high thermoelectric conversion efficiency (Bruno Miguel et.al, 2018). To synthesize CuI nanostructures, many synthetic techniques have been reported in literature like reactive sputtering, pulsed laser deposition, laser assisted molecular beam deposition, polymer assisted reaction, iodination, wet chemical synthesis and sol-gel technique (V. Y. Bokshis et.al 2004, Y. Xu et.al 2007).

Nanosized CuI is being pursued with great interest because of several possible technical applications in catalysis, drug delivery systems, separation techniques, photonics as well as piezoelectric and other dielectric devices (U. Meyer et.al, 2001). CuI has been prepared by several different methods, such as iodination of Cu films, electro deposition (T. Takeda et.al, 1997) pulse laser deposition technique (A. Tanji et.al, 2000) liquid phase reaction (P.M. Sirimanne et.al, 2003) and vacuum evaporation (K. Tennakone et.al, 1998)  $\gamma$ -CuI nanocrystals have been synthesized by an ethanol thermal method,  $\beta$ -CuI were fabricated by a hybrid electrochemical/chemical method (M.R. Penner, 2003). CuI can also be synthesized by co-precipitation, sol-gel processing, microemulsion, hydrothermal methods, solvo-thermal methods, template syntheses, biomimetic syntheses (B.L. Cushing et.al, 2004) and others. Despite the

exciting developments, finding the new route suitable for facile, scale-up synthesis and flexible experimental processing is still a current challenge to meet the demand of applications in the near future. In this study, we develop a chemical route to synthesis spherical CuI nanoparticles at room temperature. CuI nanoparticles that are prepared by this strategy show good dispersion in the suspension. CuI has been successfully applied in scintillators, organic electronics (Y. Zhou, 2012) and bipolar diodes. The developments of high quality bipolar diodes open up the application of CuI in transparent electronics. The conductivity approaches  $0.1 \Omega^{-1} \text{ cm}^{-1}$  in  $\gamma$ -phase is slightly higher in  $\beta$ -phase and in  $\alpha$ -phase it reaches higher value  $1 \Omega^{-1} \text{ cm}^{-1}$  but the  $\gamma$ -phase conductivity depends on the presence of iodine in stoichiometric excess (T. Prakash, 2011).

CuI thin films has also been prepared and deposited by various physical and chemical techniques which include reactive sputtering (K. Reichld et.al, 1978), pulsed laser deposition and electro deposition (M. Rusop et.al, 2003), laser assisted molecular beam deposition (LAMBD) (W. Wijekoon et.al, 1993), polymer assisted reaction (V. Bokshits et.al, 2003), iodination of thin copper films (M.N. Amalina et.al, 3013), wet chemical synthesis using CuO suspensions (M. Yang et.al, 2004). Other methods that have been used include vacuum evaporation (Tennakone et.al, 1998), ethanol thermal method (Y. Liu et.al, 2001), hybrid electrochemical/chemical method (H. Huang et.al, 2012), hydrothermal method (B.A. Nejjand et.al, 2014), as a composite (F. Tavakoli et.al, 2014), colloidal synthesis [M. Yongsheng et.al, 2013], green synthesis [F. Tavakoli et.al, 2013], chemical bath method, successive ionic layer adsorption and reaction (SILAR) [R.N. Bulakhe et.al, 2013] etc. Studies have shown that SILAR method produces a better structure compared to other methods of deposition. SILAR has other advantages such as low cost, low temperature and ease of deposition (H.M. Pathan et.al, 2004).

## **1.9 Applications of nanomaterials**

Consolidated nanocomposites and nanostructures enable production of ultrahigh strength, tough structural materials and novel magnets. Significant developments are taking place in the sintering of nanophase ceramic materials and in textiles and plastics containing dispersed nanoparticles. Since nanoparticles can literally be particles from any substances, they are also versatile enough and can be used in many types of technological applications, from delicate electronics to revolutionary medical procedures. Surface properties of carbon nanotubes are being explored for catalytic applications, especially after deposition of metal nanoparticles on the surface. Main applications of fields of metal oxide nanoparticles are electronics, pharmacy/medicine, cosmetics as well as chemistry and catalysis. Some universal applications of the nanoparticles are as follows (Y. Gogotsi, 2006):

### ***i) Optical applications***

Nanoparticles could be engineered and used for anti-reflection product coatings, producing a refractive index for various surfaces, and also providing light based sensors for use in diagnosing cancer. Functional devices based on quantum confinement would be of use in photonic switching and optical communications.

### ***ii) Magnetic applications***

Nanoparticles have the potential to increase the density of various storage media, and also when magnetized they can improve the detail and contrast of MRI images.

### ***iii) Thermal applications***

Specifically engineered particles could improve the transfer of heat from collectors of solar energy to their storage tanks. They could also enhance the coolant system currently used by transformers in these types of processes.



#### ***iv) Mechanical applications***

Nanoparticles could provide improvement over wear and tear resistance for almost to any mechanical device. They could also support these devices previously unseen anti-corrosion abilities, as well as creating entirely new composites and structural materials that are both lighter and stronger than those we use today.

#### ***v) Electronic applications***

Because of their tiny size, nanoparticles are inherently poised to aid in the production of high performance delicate electronics; they may provide not only materials with a high rate of conductivity, but also sleeker parts for small consumer electronics like cell phones. Potential applications of carbon nanotubes are numerous (Angelerakis, 2002). Carbon nanotubes are being used as tips in scanning microscopes and also as efficient field emitters for possible use in display devices. Since SWNTs can be metallic or semiconducting, we would expect many applications thereby exploiting the electronic structure of these materials. For example, the supercapacitance of the nanotubes can be used for applications such as electrochemical actuators. Field-effect transistors have been fabricated using nanotubes.

#### ***vi) Energy applications***

Nanoparticle batteries would be long-lasting and have a higher energy density than those we use today. Nanostructured electrode materials could improve the capacity and performance of the Li-ion batteries (Y. Gogotsi, 2006). Metal nano-particle clusters could have revolutionary applications for hydrogen storage; they could also produce extremely efficient fuel cells by acting as electrocatalysts for these devices. Nanoparticles may also pave the way for practical and renewable energy; they have already successfully demonstrated an ability to improve solar panel efficiency many times. Moreover when nanoparticles are used as catalysts in combustion

engines, they have shown properties that deliver more efficient engines and therefore more economic.

### ***vii)Biomedical applications***

Medical applications of nanoparticles are rapidly advancing. The pathogen-sized proportions of nanoparticles naturally make them prime candidates for the fight against various unwanted invaders of the human body; they can be injected into the bloodstream to fight viruses and bacteria. Nanoparticles can be equipped with sensors and cameras as well as cancer-killing drugs. They would then be able to swim through the bloodstream, using their sensors to locate the exact site of the cancer tissue. Cameras could beam back images so that they can be located on both optical imaging devices and MRI. One could track these tiny particles as they make their way through the human system and deliver doses of anti-cancer drugs to the cancer site, thereby killing off every last molecule of the tumour cells without painful and side effects or unnecessary damage. This would not only make cancer treatment much less uncomfortable for patients, but also faster and more effective. It may soon find that wounds are dressed with antibacterial coatings of silver nanoparticles. Nanoparticles have also been used to produce “quantum dots,” which can detect diseases, as well as interactive foods and drinks that change flavour and colour based on ones tastes, or in some cases may even alter their nutrient content based on person’s state of health. Colloidal gold particles attached to DNA strands can be employed to assay specific complementary DNAs. Drug and gene delivery will become increasingly more effective with the use of nanoparticles and nanocapsules [Y. Gogotsi, 2006].

### ***viii)Chemical applications***

Chemical and biochemical sensors have been fabricated with nanotubes. There are many examples where semiconductor or metal nanocrystals or quantum dots have been tagged for use

as biological sensors. Nanotechnology has given rise to house cleaning chemicals that appear to have miraculous effects; the nanoparticles inside these cleaning fluids have been engineered on the molecular level so that when they encounter unwanted dirt or grime, they “eat” it. Self-cleaning fabrics has been manufactured. The nanoparticles inside these materials have been similarly engineered to “eat” stains; in others nano-hairs have been applied in a thin, invisible layer over the fabric itself so that stains cannot penetrate and the resulting fabric is either extremely stain-resistant or virtually impossible to soil.

#### ***ix)Cosmetics/Pharmaceuticals applications***

In the range of cosmetics the most economic relevant application are nanoparticle-based sunscreens. Here nanoparticulate titania and zinc oxide are used as UV light absorbing components, which are transparent due to their small size and provide an effective protection. As a result, TiO<sub>2</sub> and ZnO are finding increasing application in sensitive skin and baby products and daily-wear skin lotions.

#### **1.10 Applications of nanomaterials as Diluted Magnetic Semiconductors**

Most recently, the field of diluted magnetic semiconductors (DMSs) has gained the attraction of the researchers due to their exclusive properties and their increasing demand in the areas of device physics such as optoelectronic and spintronics. Diluted magnetic semiconductors (DMS) are a class of magnetic semiconductors in which a fraction of the cations are substitutionally replaced by magnetic transition metal ions like Cr, Mn, Fe, Ni, or Co (having net spin) into a semiconducting host such as III–V (GaAs, GaN, etc.) and II–VI (ZnTe, ZnO, etc.) compound semiconductors (M. V. Schilfgaarde et.al 2001, H. Saito et.al 2003). A desirable change can be brought about by varying the concentration of the dopant which in turn changes the lattice constant, energy gap, magnetic and optical properties of DMS materials.

The diluted magnetic semiconductors (DMSs), which have both ferromagnetic and semiconducting properties, are a unique type of promising materials for the fast emerging field of spintronics, where conventional charge-based electronics could be replaced with devices possessing both spin and charge functionality. The possibility to manipulate the spin of the electron, as well as the charge, opens up fascinating routes for processing information and data storage (S. Wolf et.al, 2001). The spin-dependent magnetic phenomena can be manipulated in the low-dimensional tailored magnetic DMSs thin films for various spin-based devices to unprecedented capabilities (T. Fukumura et.al 2004, S. J. Pearton et.al 2005). These DMSs have recently attracted increasing attention because of their potential use in spintronic devices (B. Pal et.al, 2011).

As a consequence of the substitution of 3d transition-metal ions (some species of magnetic ions, i.e., ions bearing a net magnetic moment) for the cations of the host semiconductors, the electronic structure of the substituted 3d transition-metal impurities in semiconductors influences two competing factors: strong 3d-host hybridization and strong Coulomb interactions between 3d-3d electrons. The latter is responsible for the multiplet structures observed in d-d optical-absorption spectra. On the other hand, as specifically shown for the Mn-doped systems the hybridization between the transition-metal 3d and the host valence band gives rise to the magnetic interaction between the localized 3d spins and the carriers in the host valence band. The main challenge in the practical applications of the DMS materials is the attainment of ferromagnetism (FM) above room temperature (RT) to be compatible with junction temperatures. Dietl et al., [T. Dietl et.al, 2000] predicted the existence of high-temperature FM in some magnetically doped wide band gap semiconductors. The ferromagnetism in DMSs due to interactions between local magnetic moments of doped magnetic ions and the spins of charge

carriers in host semiconductors is known as carrier-induced ferromagnetism (T. Jungwirth et.al, 2006). The interaction among the doped magnetic ions (mediated through holes or electrons) leads to ferromagnetic order at relatively low temperatures (L. M. Sandratskii et.al, 2006). The exchange pair interactions exhibit a strong directional dependence and exponentially damped with increasing distance between doped magnetic atoms (J. Kudrnovsk' u et.al, 2004).

### **1.11 Electrochemical applications of nanomaterials**

Electrochemistry is playing a big role in all areas of science and engineering. For ex; Electroanalytical methods have potential advantages in (bio) chemical sensing and biomedical sciences. Cyclic voltammetry is a classical tool to investigate and derive the reaction mechanisms of electroactive inorganic and organic materials.

The emergence of nanoscience and nanotechnology has led to great developments in electrochemical science and technology, which led to a new branch of electrochemistry research - electrochemical nanotechnology - that combines electrochemical techniques with nanotechnologies to address important issues in energy, electronics, environment, and health care. For example, in the last decade, newly developed nanotechnologies (including electrochemical nanotechnologies) have enabled researchers to find and produce a variety of nanostructured materials with highly controlled and unique optical, magnetic, or catalytic properties. Furthermore, the diversity in composition (inorganic or organic, metals, or semiconductors), shape (particles, rods, wires, or tubes), and the readiness for surface functionalization (physical, chemical, or biological) have made it possible for various functional nanomaterials to be fabricated for sensing, electrocatalysis, energy storage and conversion. The new millennium presents opportunities as well as challenges to scientists and engineers working in the dynamic field of functional nanomaterials. The application of nanomaterials in the field of

electrochemical technology focusing on nanodevices, nanoelectronics, sensors, energy storage and conversion is on the rise. Electrochemical nanotechnologies can provide solutions to significant technical barriers and potentially revolutionize research in these emerging areas. Many areas of potential applications for nanomaterials in electrochemistry and bioelectrochemistry, is particularly useful in sensing and catalytic processes (P. T. Kissinger 2005, A. S. Santos et.al 2003).

Nanomaterials based sensing systems provide a new class of rapid and low cost detection alternatives with interest in the field of safety and security applications. In this review we report the recent trends in the use of various nanomaterials such as nanoparticles, carbon nanotubes, nanowires and graphene to detect different safety and security related analytes (i.e. microorganisms, toxins, pesticides and explosives). Nanomaterials are used either as modifiers of the electrochemical transducers or as labels with the objective to enhance the electrochemical signal, improve the stability and in general the performance of the detection systems including their cost-efficiency. Most of the developed systems are shown to bring excellent improvements while being used in the laboratory.

In general, there is a need to understand the mechanisms of formation of the nanomaterials, the accurate connections between the synthesis conditions, nanomaterial structure and properties are essential for their developments in desired applications. The ability to engineer the properties required for various applications will contribute greatly to the growth of this field and commercial applicability.