Chapter - 1

Existing Information on Nanoscience, ZnS Nanomaterials and its Applications
1.1 Introduction to nanoscience

Nanoscience and nanotechnology includes the synthesis, characterization, exploration and utilization of nanostructured materials. The application of nanomaterials can be historically traced back to even before the generation of modern science and technology.

Nanoparticles were used as dye materials in ceramics by ancient people [1]; colloidal gold was used in medical treatment for cure of dipsomania, arthritis etc, as early as from 19\textsuperscript{th} century; systematic experiments conducted on nanomaterials had also been started from the days of well known Faraday experiments [2] in the 1857. In 1959, Richard Feynman gave a lecture titled “there’s plenty of room at the bottom”, suggesting the possibility of manipulating things at atomic level [3].

This is generally considered to be the foreseeing of nanotechnology. However, the real burst of nanotechnology didn’t come until the early 1990s. In the past decades, sophisticated instruments such as scanning electron microscopy, transmission electron microscopy and scanning probe microscopy for characterization and manipulation became more available for researchers to approach the nanoworld. Device miniaturization in semiconductor industry is also a significant factor for the development of nanotechnology.

The Moore’s law predicted the performance of transistor and density double every 24 months. Nanoelectronic devices based on new nanomaterials systems and new device structures will contribute to the development of next generation of microelectronics. For example, single electron transistor [4, 5] and field effect transistor [6–8] based on single wall carbon nanotubes are already on the way. The developments in quantum physics and the emergence of new fields like soft condensed matter physics all gave a new dimension to the wide area of materials science. The earlier notion of change in material properties by change in composition or mixing of different materials remained no more isolated and a radically different approach emerged in which, material properties are engineered by changing the size by keeping the chemical composition intact [9,10]. The methodology of varying the material characteristics with size is feasible only in a
specific size regime, namely nanometer \(10^{-9}\) meter, where a quantum swapping of classical phenomena can be observed. This gave birth to a new branch of science and technology called 'nanoscience' and 'nanotechnology'.

Nanotechnology deals with materials or structures in nanometer scales, typically ranging from sub nanometers to several hundred nanometers. One nanometer is \(10^{-3}\) micrometer or \(10^{-9}\) meter. Nanotechnology is the design, fabrication and application of nanostructures or nanomaterials, and the fundamental understanding of the relationships between physical properties or phenomena and material dimensions. Nanotechnology is a new field or a new scientific domain. Similar to quantum mechanics, on nanometer scale, materials or structures may possess new physical properties or exhibit new physical phenomena. Some of these properties are already known.

For example, band gap of semiconductors can be tuned by varying material dimension. There may be many more unique physical properties not known to us yet. These new physical properties or phenomena will not only satisfy everlasting human curiosity, but also promise new advancement in technology. Another very important aspect of nanotechnology is the miniaturization of current and new instruments, sensors and machines that will greatly impact the world we live in. Examples of possible miniaturization are: computers with infinitely great power that compute algorithms to mimic human brains, biosensors that warn us at the early stage of the onset of disease and preferably at the molecular level and target specific drugs that automatically attack the diseased cells on site, nanorobots that can repair internal damage and remove chemical toxins in human bodies, and nanoscaled electronics that constantly monitor our local environment. Further, nanotechnology is also expanded extensively to other fields due to the novel properties of nanomaterials discovered and to be discovered. For example, nanowires can be potentially used in nanophotonics, laser \[11\], nanoelectronics \[12\], solar cells \[13\], resonators \[14\] and high sensitivity sensors \[15\]. Nanoparticles can be potentially used in catalysts \[16\], functional coatings, nanoelectronics \[17\], energy storage \[18\], drug delivery \[19\] and biomedicines \[20\]. Nanostructured thin films can be used in light emitting devices, displays and high efficiency photovoltaics. These are only a limited part of the fast developing
nanotechnology, yet numerous of other potential applications of nanomaterials have already been or will be discovered. Nanotechnology is an interdisciplinary research field in which many physicists, chemists, biologists, materials scientist and other specialists are involved.

The term of nanomaterials covers various types of nanosturctured materials which posses at least one dimension in the nanometer range. Various nanostructures which include zero dimension nanostructures such as metallic, semiconducting and ceramic nanoparticles; one dimension nanostructures such nanowires, nanotubes and nanorods; two dimension nanostructures such as quantum well structures. Besides this individual nanostructures, ensembles of these nanostructures form high dimension arrays, assemblies, and superlattices. The properties of materials with nanometer dimensions are significantly different from those of atoms and bulk 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 [21].

Due to their small dimensions, nanomaterials have extremely large surface area to volume ratio, which makes a large fraction of atoms of the materials to be on the surface or interfacial atoms, resulting in more surface dependent material properties. Especially when the sizes of nanomaterials are comparable to Debye length, the entire material will be affected by the surface properties of nanomaterials [22, 23]. This in turn may enhance or modify the properties of the bulk materials. For example, metallic nanoparticles can be used as very active catalysts. Chemical sensors from nanoparticles and nanowires enhanced the sensitivity and sensor selectivity. The quantum confinement of nanomaterials has profound effects on the properties of nanomaterials. The energy band structure and charge carrier density in the materials can be modified quite differently from their bulk counterpart and this in turn will modify the electronic and optical properties of the materials. Nanotechnology has an extremely broad range of potential applications in nanoscale electronics, optics, nanobiological systems, nanomedicine etc. Therefore it requires formation and contribution from multidisciplinary teams of physicists, chemists, materials scientists, engineers,
molecular biologists, pharmacologists and others to work together on (i) synthesis and processing of nanomaterials and nanostructures, (ii) understanding the physical properties related to the nanometer scale, (iii) design and fabrication of nano-devices or devices with nanomaterials as building blocks, and (iv) design and construction of novel tools for characterization of nanostructures and nanomaterials.

Synthesis and processing of nanomaterials and nanostructures are the essential aspect of nanotechnology. Studies on new physical properties and applications of nanomaterials and nanostructures are possible only when nanostructured materials are made available with desired size, morphology, crystal and microstructure and chemical composition. Work on the fabrication and processing of nanomaterials and nanostructures started long time ago, far earlier than nanotechnology emerged as a new scientific field. Such research has been drastically intensified in the last decade, resulting in overwhelming literatures in many journals across different disciplines.

The research on nanotechnology is evolving and expanding very rapidly. There are two principal ways of manufacturing nanoscale materials; the top-down nanofabrication starts with a large structure and proceeds to make it smaller through successive cuttings while the bottom-up nanofabrication starts with individual atoms and builds them up to a nanostructure. When we bring constituents of materials down to the nanoscale, the properties change. Some materials used for electrical insulations can become conductive and other materials can become transparent or soluble.

For example gold nanoparticles have a different colour, melting point and chemical properties, due to the nature of the interactions among the atoms that make up the gold, as compared to a nugget of gold. Nano gold does not look like bulk gold, the nanoscale particles can be orange, purple, red or greenish depending on the size of the particle. All these new properties that open up when bringing the material down in scale is of great interest for the industry and society as it enables new applications and products. Nanotechnology is considered by some to be the next industrial revolution and is believed to cause enormous
impacts on the society, economy and life in general in the future. Nanotechnology have wide application in medicine, information technology, biotechnology, energy production and storage, material technology, manufacturing, instrumentation, environmental applications and security.

Lasers and light emitting diodes (LED) from both quantum dots and quantum wires are very promising in the future developments of optoelectronics. High density information storage using quantum dot devices is also a fast developing area. Reduced imperfections are also an important factor in determination of the properties of the nanomaterials. Nanosturctures and nanomaterials favours of a self-purification process in that the impurities and intrinsic material defects will move to near the surface upon thermal annealing. This increased materials perfection affects the properties of nanomaterials. For example, the chemical stability for certain nanomaterials may be enhanced, the mechanical properties of nanomaterials will be better than the bulk materials.

1.2 Size effect at nanoscale

When the piece of material is so small that the surface bonds dominate over the bulk bonds, the material promotes the nano-size effect due to the unsatisfied bonds of the outermost atoms at any crystal. In the bulk those effects are compensated with in a crystal by strained lattice parameters of the surface atoms with their next to last atoms. Semiconductor quantum dots, also known as nanocrystals or nanoparticles, are a special class of materials whose crystals are composed of periodic groups of II-VI, III-V or IV-VI materials. The most notable and interesting property of semiconductor nanoparticles is the distinct large magnitude change in optical properties as a function of particle size. The three-dimensional quantum-size effect, leading to an increase in band gap with a decrease in particle size, is well known for colloidal semiconductor sols where the individual colloidal particles are dispersed in a liquid or glass [24].

Quantum confinement effect is defined as the increase in band gap of a semiconductor material as the particle size decreases. It is caused by localization of electrons and holes in a confined space resulting in observable quantization of
the energy levels of the electrons and holes. The idea behind confinement is all about keeping electrons and holes trapped in a small area. For effective confinement, the particle sizes have to be less than 30 nm [25]. Quantum confinement comes in several forms which include 2-D (two dimensional) confinement, which is only restricted in one dimension, and the result is a quantum well (or plane), and these are what most lasers are currently built from.

![Figure 1.1 Schematic illustration of density of states of a semiconductor as a function of dimension.](image)

1-D confinement occurs in nanowires and 0-D confinement is found only in the quantum dot. A quantum dot exhibits 0-D confinement, meaning that electrons are confined in all three dimensions. So a quantum dot can be loosely described as an artificial atom [26, 27] because of the discretization of conduction and valence bands caused by quantum confinement of charge-carriers. This achievement is very important since we cannot readily experiment on regular atoms because they are too small and too difficult to isolate in an experiment.

Quantum confinement is vitally important for one thing, it leads to new electronic properties that are not present in today’s semiconductor devices. The density of states functions plotted against energy for bulk (3-D), 2-D, 1-D and 0-D are
shown in Figure 1.1. The continuous energy levels of the bulk and the discrete energy levels for quantum dots (0-D) are apparent in this Figure1.1. In semiconductors, an electron-hole pair is created when an electron leaves the valence band and enters the conduction band due to excitation. An exciton is created when a weak attraction force (Coulombic force) between the hole and electron exists.

![Figure 1.1](image)

**Figure 1.2** Energy Dispersion for the (a) 3-D bulk semiconductor case compared to that of the (b) 0-D Quantum Dot case [29].

It may be bound or moving in a crystal conveying energy. Luminescence may result from the recombination of the electron and the hole. Excitons have a natural physical separation that varies from semiconductor to semiconductor. This average separation distance is termed Exciton Bohr Radius. In bulk, the dimensions of the semiconductor crystal are much larger than the Excitonic Bohr Radius, allowing the exciton to extend to its natural limit [28]. The energy levels of a bulk semiconductor are very close together such that they are described as continuous, meaning that there is almost no energy difference between them, as shown in Figure 1.2(a) [29]. Since the band-gap of the bulk semiconductor is fixed, the transitions result in fixed emission frequencies. However, if the sizes of a semiconductor particle are comparable or small enough that they approach the size of the materials bulk Exciton Bohr Radius, then the continuum states are broken down into discrete states and can no longer be treated as continuous,
meaning that there is a small and finite separation between energy levels as shown in Figure 1.2(b). This result in a large effective band gap and leads to an optical transition which is blue-shifted from that of bulk materials [30, 31].

1.3 Properties of materials at nanoscale

1.3.1 Optical properties

The reduction of materials’ dimension has pronounced effects on the optical properties. The size dependence can be generally classified into two groups. One is due to the increased energy level spacing as the system becomes more confined, and the other is related to surface plasmon resonance. The quantum size effect is most pronounced for semiconductor nanoparticles, where the band gap increases with a decreasing size, resulting in the interband transition shifting to higher frequencies [32,33]. In a semiconductor, the energy separation, i.e. the energy difference between the completely filled valence band and the empty conduction band is of the order of a few electron volts and increases rapidly with a decreasing size [33].

Quantum confinement produces a blue shift in the band gap as well as appearance of discrete subbands corresponding to quantization along the direction of confinement. The optical properties of nanostructured semiconductors are highly size dependent and thus can be modified by varying the size alone, keeping the chemical composition intact. The luminescent emission from the semiconductor nanostructures can be tuned by varying size of the nanoparticles. In the case of nanostructured semiconductor lasers, the carrier confinement and nature of electronic density of states of the nanostructures make it more efficient for devices operating at lower threshold currents than lasers with bulk materials. The size dependent emission spectra of quantum wells, quantum wires and quantum dots make them attractive lasing media. The performance of quantum dot lasers is less temperature dependent than conventional semiconductor lasers [34]. The same quantum size effect is also known for metal nanoparticles. However, in order to observe the localization of the energy levels, the size must be very small, as the level spacing has to exceed the thermal energy (∼26 meV). Surface plasmon
resonance is the coherent collective excitation of all the free electrons within the conduction band, leading to an in-phase oscillation [35, 36]. When the size of a metal nanocrystal is smaller than the wavelength of incident radiation, a surface plasmon resonance is generated [37]. The energy of the surface plasmon resonance depends on both the free electron density and the dielectric medium surrounding the nanoparticle. The width of the resonance varies with the characteristic time before electron scattering. For larger nanoparticle, the resonance sharpens as the scattering length increases. Noble metals have the resonance frequency in the visible range of electromagnetic spectrum.

1.3.2 Electronic properties

The changes which occur in electronic properties as the system length scale is reduced are related mainly to the increasing influence of the wave-like property of the electrons (quantum mechanical effects) and the scarcity of scattering centres. As the size of the system becomes comparable with the de Broglie wavelength of the electrons, the discrete nature of the energy states becomes apparent once again, although a fully discrete energy spectrum is only observed in systems that are confined in all three dimensions. In certain cases, conducting materials become insulators below a critical length scale, as the energy bands cease to overlap. Owing to their intrinsic wave-like nature, electrons can tunnel quantum mechanically between two closely adjacent nanostructures, and if a voltage is applied between two nanostructures which aligns the discrete energy levels in the DOS, resonant tunneling occurs, which abruptly increases the tunneling current. In macroscopic systems, electronic transport is determined primarily by scattering with phonons, impurities or other carriers or by scattering at rough interfaces. The path of each electron resembles a random walk, and transport is said to be diffusive. When the system dimensions are smaller than the electron mean free path for inelastic scattering, electrons can travel through the system without randomization of the phase of their wave functions.

This gives rise to additional localization phenomena which are specifically related to phase interference. If the system is sufficiently small so that all scattering centres can be eliminated completely, and if the sample boundaries are smooth so
that boundary reflections are purely specular, then electron transport becomes purely ballistic, with the sample acting as a waveguide for the electron wave function.

Conduction in highly confined structures, such as quantum dots, is very sensitive to the presence of other charge carriers and hence the charge state of the dot. These Coulomb blockade effects result in conduction processes involving single electrons and as a result they require only a small amount of energy to operate a switch, transistor or memory element. All these phenomena can be utilized to produce radically different types of components for electronic, optoelectronic and information processing applications, such as resonant tunneling transistors and single-electron transistors.

1.3.3 Chemical properties

The change in structure as a function of particle size is intrinsically linked to the changes in electronic properties. The ionization potential (the energy required to remove an electron) is generally higher for small atomic clusters than for the corresponding bulk material. Furthermore, the ionization potential exhibits marked fluctuations as a function of cluster size. Such effects appear to be linked to chemical reactivity of the materials. Nanoscale structures such as nanoparticles and nanolayers have very high surface area to volume ratios and potentially different crystallographic structures which may lead to a radical alteration in chemical reactivity. Catalysis using finely divided nanoscale systems can increase the rate, selectivity and efficiency of chemical reactions such as combustion or synthesis whilst simultaneously, significantly reducing waste and pollution. Nanoparticles often exhibit new chemistry as distinct from their larger particulate counterparts; for example, many new medicines are insoluble in water when in the form of micron-sized particles but will dissolve easily when in a nanostructured form [38].

1.3.4 Structural properties

The increase in surface area and surface energy with decreasing particle size leads to changes in interatomic spacings. For Cu metallic clusters the interatomic
spacing is observed to be decreasing with decreasing cluster size. This is due to the compressive strain induced by the internal pressure arising from the small radius of curvature in the nanoparticle. Conversely, for semiconductors and metal oxides there is evidence that interatomic spacings increase with decreasing particle size.

A further effect is the apparent stability of metastable structures in small nanoparticles and clusters, such that all traces of the usual bulk atomic arrangement is lost. Metallic nanoparticles, such as gold, are known to adopt polyhedral shapes such as cubeoctahedra, multiply twinned icosahedra and multiply twinned decahedra.

These nanoparticles may be regarded as multiply twinned crystalline particles (MTPs) in which the shapes can be understood in terms of the surface energies of various crystallographic planes, the growth rates along various crystallographic directions and the energy required for the formation of defects such as twin boundaries. However, there is compelling evidence that such particles are not crystals but are quasi periodic crystals or crystalloids. These icosahedral and decahedral quasi crystals form the basis for further growth of the nanocluster, upto a size where they will switch into more regular crystalline packing arrangements.

Crystalline solids are distinct from amorphous solids in that they possess long-range periodic order and the patterns and symmetries which occur correspond to those of the 230 space groups. Quasiperiodic crystals do not possess such long-range periodic order and are distinct in that they exhibit fivefold symmetry, which is forbidden in the 230 space groups. In the cubic close-packed and hexagonal close-packed structures, exhibited by many metals, each atom is coordinated by 12 neighbouring atoms.

All of the coordinating atoms are in contact, although not evenly distributed around the central atom. However, there is an alternative arrangement in which each coordinating atom is situated at the apex of an icosahedron and in contact only with the central atom. If however we relax this rigid atomic sphere model and allow the central atom to reduce in diameter by 10%, the coordinating atoms come into contact and the body now has the shape and symmetry of a regular
icosahedron with point group symmetry 235, indicating the presence of 30 two-fold, 20 threefold and 12 fivefold axes of symmetry.

This geometry represents the nucleus of a quasiperiodic crystal which may grow in the forms of icosahedra or pentagonal dodecahedra. These are dual solids with identical symmetry, the apices of one being replaced by the faces of the other. The size-related instability characteristics of quasiperiodic crystals are not well understood. A frequently observed process appears to be that of multiple twinning, such crystals being distinguished from quasiperiodic crystals by their electron diffraction patterns. Here the five triangular faces of the fivefold symmetric icosahedron can be mimicked by five twin-related tetrahedra (with a close-packed crystalline structure) through relatively small atomic movements [38].

1.3.5 Thermal properties

By controlling the structures of materials at nanoscale dimensions, the properties of the nanostructures can be controlled and tailored in a very predictable manner to meet the needs for a variety of applications. The engineered nanostructures include metallic and non-metallic nanoparticles, nanotubes, quantum dots and superlattices, thin films, nano composites and nanoelectronic and optoelectronic devices which utilize the superior properties of the nanomaterials to fulfill the applications.

Many properties of the nanoscale materials have been well studied, including the optical electrical, magnetic and mechanical properties. However, the studies on thermal properties of nanomaterials have only seen slower progresses. This is partially due to the difficulties of experimentally measuring and controlling the thermal transport in nanoscale dimensions. Atomic force microscope (AFM) has been introduced to measure the thermal transport of nanostructures with nanometer-scale high spatial resolution, providing a promising way to probe the thermal properties with nanostructures [39]. Moreover, the theoretical simulations and analysis of thermal transport in nanostructures are still in infancy. As the dimensions go down into nanoscale, the availability of the definition of
temperature is in question. In non-metallic material system, the thermal energy is mainly carried by phonons, which have a wide variation in frequency and the mean free paths. The heat carrying phonons often have large wave vectors and mean free path in the order of nanometer range at room temperature, so that the dimensions of the nanostructures are comparable to the mean free path and wavelength of phonons. However the general definition of temperature is based on the average energy of a material system in equilibrium.

For macroscopic systems, the dimension is large enough to define a local temperature in each region within the materials and this local temperature will vary from region to region, so that one can study the thermal transport properties of the materials based on certain temperature distributions of the materials. But for nanomaterial systems, the dimensions may be too small to define a local temperature. Moreover, it is also problematic to use the concept of temperature which is defined in equilibrium conditions, for the non equilibrium processes of thermal transport in nanomaterials, posing difficulties for theoretical analysis of thermal transport in nanoscales [39].

In nanomaterials systems, several factors such as the small size, the special shape, the large interfaces modify the thermal properties of the nanomaterials, rendering them the quite different behavior as compared to the macroscopic materials. As the dimension goes down to nanoscales, the size of the nanomaterials is comparable to the wavelength and the mean free path of the phonons, so that the phonon transport within the materials will be changed significantly due the phonon confinement and quantization of phonon transport, resulting in modified thermal properties.

The special structure of nanomaterials also affects the thermal properties. For example, because of the tubular structures of carbon nanotubes, they have extremely high thermal conductivity in axial directions, leaving high anisotropy in the heat transport in the materials [40].

The interfaces are also a very important factor for determining the thermal properties of nanomaterials. The use of nanofluid to enhance the thermal transport
is another promising application of the thermal properties of nanomaterials. Nanofluids are generally referred to the solid-liquid composite materials, which consist of nanomaterials of size in the range 1-100nm suspended in a liquid. Nanofluids hold increasing attentions in both research and practical applications due to their greatly enhanced thermal properties compared to their base fluids.

Many type of nanomaterials can be used in nanofluids including nanoparticles of oxides, nitrides, metals, metal carbides, and nanofibers such as single walled and multiwalled carbon nanotubes, which can be dispersed in to a variety of base liquid depending on the possible applications, such as water, ethylene glycol, and oils. The most important features of nanofluids are the significant increase of thermal conductivity compared with liquids without nanomaterials.

1.3.6 Mechanical properties

Due to the nanometer size, many of the mechanical properties of the nanomaterials are different from the bulk materials including the hardness, elastic modulus, fracture toughness, scratch resistance and fatigue strength etc. An enhancement of mechanical properties of nanomaterials can result due to this modification, which are generally resulting from structural perfection of the materials [41, 42].

The small size either renders them free of internal structural imperfections such as dislocations, micro twins, and impurity precipitates or the few defects or impurities present cannot multiply sufficiently to cause mechanical failure. The imperfections within the nano dimension are highly energetic and will migrate to the surface to relax themselves under annealing, purifying the material and leaving perfect material structures inside the nanomaterials. Moreover, the external surfaces of nanomaterials also have less or free of defects compared to bulk materials. Introduction to nanotechnology materials, serving to enhance the mechanical properties of nanomaterials [41].

The enhanced mechanical properties of the nanomaterials could have many potential applications both in nanoscale such as mechanical nano resonators,
sensors, microscope probe tips and nanotweezers for nanoscale object manipulation, light weight high strength materials, flexible conductive coatings, wear resistance coatings, tougher and harder cutting tools etc. Among many of the novel mechanical properties of nanomaterials, high hardness has been observed for many nanomaterials. A variety of super hard nanocomposites can be made of nitrides, borides and carbides by plasma induced chemical and physical vapor deposition [43]. The excellent mechanical properties of nanomaterials could lead to many potential applications in all the nano, micro and macro scales. High frequency electro-mechanical resonators have been made from carbon nanotubes and nanowires. Nanostructured materials can also be used as nanoprobe or nanotweezers to probe and manipulate nanomaterials in a nanometer range [44].

Due to their high aspect ratio and small dimensions, one-dimensional nanostructures such as carbon nanotubes can also be used as nano probe tips. The nanotweezers can be made from two individual carbon nanotubes. This nanotweezers operated under electrical stimulus was used to probe the electrical characteristics of nanostructures. It could be useful both in the nanostructure characterization and the manipulation. The nanotweezers could be used as a novel electromechanical sensor that can detect pressure or viscosity of media by measuring the change in resonance frequency and Q-factor of the device. They can also be explored into manipulation and modification of biological systems such as structures within a cell.

1.4 Brief Overview of ZnS and its properties

ZnS has two commonly available allotropes: one with a Zinc blend (ZB) structure and another one with a Wurtzite (WZ) structure. The cubic form is the stable low-temperature phase, while the latter is the high-temperature polymorph which forms at around 1296 K [45].

For the purpose of comparison, Figure 1.3 shows three different views of these structures. The differences can be described either in terms of the relative handedness of the fourth interatomic bond or by their dihedral conformations. Alternatively, ZB consists of tetrahedrally coordinated zinc and sulfur atoms.
stacked in the ABCABC pattern, while in WZ, the same building blocks are stacked in the ABABAB pattern. The lattice parameters of ZB are \( a=b=c=5.41\ \text{Å}, \ Z=4\) (space group \( F4 \cdot 3 \text{m} \)) and that of WZ are \( a=b=3.82\ \text{Å}, \ c=6.26\ \text{Å}, \ Z=2\) (space group = \( P6_3mc \)). Such minute difference in atomic arrangements leads to large difference in properties in these materials [45], e.g. electronic structures and bandgaps. The WZ phase has a higher bandgap of 3.77 eV [46] while the ZB structure of 3.72 eV [47].

Figure 1.3 Models showing the difference between wurtzite and zinc blende crystal structures. (a and b) Show handedness of the fourth interatomic bond along the right (R) for wurtzite and along the left (L) for zinc blende. (c and d) The respective eclipsed and staggered dihedral conformations. (e and f) Show atomic arrangement along the close packing axis [48].

The band structure of a solid describes ranges of energy that an electron is “forbidden” or “allowed” to have and it determines important electronic and optical properties of the material. The optical spectra are related to band structure, its dispersion and probabilities of inter-band optical transitions. Experimentally, it
has been shown that the optical properties of the ZnS ZB and WZ phases are distinct. In order to understand such differences, electronic structures of these phases have been widely investigated [49-53].

**Figure 1.4** Band dispersions for the ZnS ZB and the WZ phases obtained using density functional theory (DFT) calculations [48]

**Figure 1.4** depicts typical band dispersions for the ZnS ZB and the WZ phases obtained using density functional theory (DFT) calculations. It can be seen that the conduction-band minima are much more dispersive than the valence band maxima for both phases. The authors further state that mobility of electrons in these materials is therefore higher than that of holes [49]. Also, p-electrons forming the top most valence band states tightly bind to sulfur and make the valence band holes less mobile. Hence, the contribution of the holes to the conductivity is expected to be smaller. The valence band comprises of three regions: a lower region consists of the s bands of Zn and S, a higher-lying region contains well localized Zn 3d bands, and a top broader band originating from the S–p states hybridized with Zn 3d states.

Notably, the phase transition temperature for the two allotropes, the bandgap and electronic structure considerably change when the size of the ZnS particles is of the order of nanometers. In an elegant and simple experiment, Qadri and co-workers used 2.7 nm ZnS ZB nanocrystals and heated them at various temperatures [54]. X-ray diffraction (XRD) measurement of these sample showed that ZB nanocrystals start converting to the WZ phase at a temperature as low as
400°C (Figure 1.5). During annealing, the particle size, cell volume, lattice parameters also changed considerably, as depicted in Table 1.1. Akiyama and co-workers using empirical calculations have demonstrated that when the sizes of the ZnS nanostructures reduce to just a few nanometers, the high temperature WZ structure becomes stabilized [55].

Figure 1.5 XRD patterns of the ZnS nanocrystals annealed at various temperatures taken with Cu Kα radiation. Peaks labeled with ZB and WZ correspond to the zinc blende and wurtzite structures, respectively [48].

They calculated cohesive energies for nanowires with ZB and WZ (hexagonal, H) structures and demonstrated that the stability of a crystal structure depends on the nanowire diameter. Figure 1.6 shows the plot of energy differences between 6H and ZB structures $\Delta E_{6H-ZB}$, 4H and ZB structures $\Delta E_{4H-ZB}$, and WZ and ZB structures $\Delta E_{WZ-ZB}$ of ZnS nanowires as functions of nanowire diameters. As seen in the plot, the energy differences converge into those of the bulk phase as diameter increases, indicating the appearance of bulk features at a large diameter.

The WZ structure was found favorable for diameters less than 4 nm. On the other hand, the ZB structure, which is the most stable structure in the bulk, is favorable for diameters above 24 nm. The authors explained this behavior on the basis of two- and three-coordinated surface atoms on nanowire facets. Different from the fourfold coordination in the bulk solid, the Zn and S atoms at the side surfaces of WZ-ZnS nanowires are all threefold coordinated with one unsaturated bond.
Table 1.1  Calculated values of the unit-cell parameters, specific volumes, and particle sizes of the ZnS particles obtained at various annealing temperatures [48].

<table>
<thead>
<tr>
<th>Annealing Temp (°C)</th>
<th>Structure</th>
<th>% of Phase</th>
<th>Lattice parameter (Å)</th>
<th>Specific Volume (Å³)</th>
<th>Particle Size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>23°C</td>
<td>Zinc blende</td>
<td>100</td>
<td>a = 5.42 ± 0.01</td>
<td>38.8 ± 0.3</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c = 5.28 ± 0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>300°C</td>
<td>Zinc blende</td>
<td>100</td>
<td>a = 5.42 ± 0.01</td>
<td>38.7 ± 0.2</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c = 5.27 ± 0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>350°C</td>
<td>Zinc blende</td>
<td>100</td>
<td>a = 5.41 ± 0.01</td>
<td>35.7 ± 0.3</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c = 5.29 ± 0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>400°C</td>
<td>Zinc blende</td>
<td>72</td>
<td>a = 5.404 ± 0.012</td>
<td>39.5 ± 0.3</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>Wurtzite</td>
<td>28</td>
<td>a = 3.52 c = 6.26</td>
<td>39.5</td>
<td>74</td>
</tr>
<tr>
<td>500°C</td>
<td>Zinc blende</td>
<td>72</td>
<td>c = 5.41</td>
<td>39.6</td>
<td>232</td>
</tr>
<tr>
<td>500°C</td>
<td>Wurtzite</td>
<td>28</td>
<td>a = 3.82 c = 6.26</td>
<td>39.6</td>
<td>243</td>
</tr>
</tbody>
</table>

In the case of the ZB-ZnS nanowires, in addition to the threefold coordinated atom, there are also certain twofold coordinated atoms located at the edges of the nanowires facets. This makes the surface energy of ZB-ZnS nanowires larger than that of WZ-ZnS nanowires, which results in the lower stability. Therefore, when the size of the nanostructure is small so that a large number of constituting atoms
reside on the surface, it prefers to be in the WZ phase with a fewer number of dangling bonds.

Different theoretical models have been developed in order to understand the electronic properties of ZnS nanostructures [46, 56-58]. Wang and co-workers calculated the energy bandgaps of WZ-ZnS nanowires using DFT [18]. They showed that the ZnS nanowires have wider bandgaps than that of bulk ZnS crystal. The bandgap decreases with increasing diameter.

1.5 Properties of ZnS nanoparticles.

1.5.1 Luminescence

Luminescence is the generation of light. As pointed out in a recent review[59], light can be emitted via a number of luminescent processes, which include photoluminescence (PL), cathodoluminescence (CL), electroluminescence (EL), electrochemiluminescence (ECL), and thermoluminescence (TL). Table 1.2 lists typical types of luminescence and their origins. In this section, we present some typical luminescence properties of ZnS nanostructures.

Table 1.2 Different types of luminescence [59].

<table>
<thead>
<tr>
<th>Luminescence</th>
<th>Caused by</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photoluminescence (PL)</td>
<td>Photo-excitation of compounds</td>
</tr>
<tr>
<td>Cathodoluminescence (CL)</td>
<td>Electron-excitation of compounds</td>
</tr>
<tr>
<td>Electroluminescence (EL)</td>
<td>Radiative recombination of electrons and holes in a materials after an electrical current passes through them or a strong electric field is applied</td>
</tr>
<tr>
<td>Electrochemiluminescence (ECL)</td>
<td>Electrogenerated chemical excitation</td>
</tr>
<tr>
<td>Thermoluminescence (TL)</td>
<td>Detrapping process caused by heating or thermostimulation</td>
</tr>
</tbody>
</table>

ZnS exhibits direct bandgaps of 3.72 eV for the cubic ZB phase and 3.77 eV for the hexagonal WZ phase with a large exciton energy of 39 meV [60]. The strong exciton binding energy, which is much larger that that of GaN (25 meV) and the
thermal energy at room temperature (26 meV) can ensure an efficient exciton emission at RT under low excitation energy. Although much research has been devoted to the PL properties of 1D ZnS nanostructures, very few studies have reported possible UV bandgap emission at RT. This is mainly due to high sensitivity of the 1D ZnS nanostructure optical properties to the synthetic conditions, its crystal size and shape, and intrinsic defects such as vacancies and interstitials.

1.5.2 Effect of doping on optical properties

ZnS doped with manganese without changing their crystallography exhibits attractive light-emitting properties with increased optically active sites for applications as efficient phosphors [61].

All of these properties make ZnS one dimensional nanostructures attractive candidates for use in devices and other technological applications. ZnS is also an important phosphor host lattice material used in electro-luminescent devices (ELD), because of the band gap large enough to emit visible light without absorption and the efficient transport of high energy electrons [62]. Bhargava et al. [63] first reported luminescence properties of manganese doped ZnS nanocrystals prepared by a chemical process at room temperature, which initiated investigation on luminescent ZnS nanostructures. ZnS nanobelts doped with manganese were synthesized by hydrogen-assisted thermal evaporation and exhibited lasing action.

ZnS nanostructures synthesized by chemical vapor deposition (CVD) have a large number of defects, perhaps due to oxygen incorporation [64]. Nath et. al studied the green luminescence of ZnS and ZnS:Cu quantum dots embedded in zeolite matrix [65]. This study demonstrates the technological importance of semiconductor quantum dots prepared by low cost chemical route. Manzoor et. al [66] reported the growth of Cu\(^+\)-Al\(^{3+}\) and Cu\(^+\)-Al\(^{3+}\)-Mn\(^{2+}\) doped ZnS nanoparticles by wet chemical method for electroluminescent applications. The high fluorescent efficiency and dispersion in water makes ZnS nanoparticles an ideal candidate for biological labeling. Various dopants used by researchers and their optical response is displayed in Table 1.3.
Table 1.3 Optical properties of doped ZnS [48]

<table>
<thead>
<tr>
<th>Nanostructures</th>
<th>PL peaks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn/Cu-co-doped,</td>
<td>580 nm: Mn$^{2+}$-4$T_{1g}$-6$A_1$ transition;</td>
<td>[67]</td>
</tr>
<tr>
<td>Mn/Cu/Feco-doped1D</td>
<td>520 nm: Cu$^{2+}$ CB(ZnS)-$t_2$(Cu$^{2+}$(d$^9$))transition;</td>
<td></td>
</tr>
<tr>
<td>ZnS NSs</td>
<td>622 nm: Cu impurities;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>450 nm: trapped luminescence from the surface states;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>375 nm: hole traps of unsaturated sp$^3$ orbitals of the surface S atoms</td>
<td></td>
</tr>
<tr>
<td>Eu-ZnS NWs</td>
<td>520 nm: Eu$^{2+}$4f$^5$5d$^1$-4f$^6$ intra-ion transition</td>
<td>[68]</td>
</tr>
<tr>
<td>Mn-ZnS NBs</td>
<td>580 nm: Mn$^{2+}$-4$T_{1g}$-6$A_1$ transition;</td>
<td>[69]</td>
</tr>
<tr>
<td></td>
<td>450 nm: defect-related of ZnS host</td>
<td></td>
</tr>
<tr>
<td>Mn/Cd-co-ZnS 1D NSs</td>
<td>580 nm: Mn$^{2+}$-4$T_{1g}$-6$A_1$ d-d transition;</td>
<td>[70]</td>
</tr>
<tr>
<td></td>
<td>512 nm: E (splitting energy at CB)-De(Cd vacancies) transition;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>636 nm: Mn$^{2+}$-4$T_{1g}$-Cd De transition;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>440 nm: S vacancies;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>375 nm: hole traps of unsaturated sp$^3$ orbitals of the surface S atoms</td>
<td></td>
</tr>
<tr>
<td>Mn-ZnS Nanoclusters</td>
<td>580 nm: Mn$^{2+}$-4$T_{1g}$-6$A_1$ transition</td>
<td>[71]</td>
</tr>
<tr>
<td>Mn-ZnS NCs</td>
<td>585 nm: Mn$^{2+}$-4$T_{1g}$-6$A_1$ transition</td>
<td>[72]</td>
</tr>
<tr>
<td>Cu-ZnS NRs</td>
<td>565 nm: CB DL (deep localized donor level near CB)-t$_2$(Cu$^{2+}$(d$^9$)) transition;</td>
<td>[73]</td>
</tr>
<tr>
<td></td>
<td>500 nm: surface S elements;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>730 nm: deep trap states in the ZnS lattice</td>
<td></td>
</tr>
<tr>
<td>Ni-ZnS NCs</td>
<td>520 nm: d-d optical transition of Ni$^{2+}$</td>
<td>[74]</td>
</tr>
<tr>
<td>Co-ZnS NCs</td>
<td>459 nm: Vs(S vacancy)-Dopant level (Co)</td>
<td>[75]</td>
</tr>
<tr>
<td>Mn, Fe-ZnS NWs</td>
<td>580 nm: Mn$^{2+}$-4$T_{1g}$-6$A_1$ transition</td>
<td>[76]</td>
</tr>
<tr>
<td></td>
<td>520 nm: Fe doping</td>
<td></td>
</tr>
</tbody>
</table>

1.5.3 Electrical properties

According to the theory of electron scattering in solids, the electrical resistivity of nanocrystalline materials is expected to be higher than that in the coarse grained ones due to the increase in volume fraction of atoms lying in the grain boundaries. The electrical resistivity of nanocrystalline materials is also found to be higher than that of amorphous solids [77]. The variation of electrical resistivity with temperature and grain size has been determined experimentally in several nanocrystalline samples. By reducing grain size, the dielectric properties are liable.
to change dramatically. The increased grain boundary resistivity of nanocrystalline material may lead to a wide range of interesting device application. In nanomaterials, large number of grain boundaries and their insulating layers over the crystallites act as barriers to the electrical conduction and these barriers are responsible for the nonlinear characteristics. Materials with grain sizes in the nanometer range show a dispersion of the conductivity and at low frequencies the conductivity becomes strongly frequency dependent. Reduction in grain size leads to an enhancement in the volume fraction of atoms/ions and defect in the grain boundaries. In nanomaterials, the high volume fraction of atoms in the grain boundaries seems to cause a universal behavior in the nanocrystalline materials.

1.5.4 Magnetic Properties

Superparamagnetism is one of the important properties of nanomaterials. Ferromagnetic particles become unstable when the particle size reduces below a certain size, since the surface energy provides a sufficient energy for domains to spontaneously switch polarization directions. As a result ferromagnetics become paramagnetics. However, nanometer sized ferromagnetic turned to paramagnetic behaves differently from the conventional paramagnetic and is referred to as superparamagnetism [78].

1.5.5 Thermal properties

Nanoparticles of semiconductors are found to have lower melting temperatures as compared with their bulk forms, when the particle size decreases below 100 nm. The lowering of the meltingpoints is explained by the fact that the surface energy increases with a decreasing size. The decrease in the phase transition temperature can be attributed to the changes in the ratio of surface energy to volume energy as a function of particle size [79].

1.5.6 Mechanical properties

The mechanical properties of materials increase with a decreasing size. Thermodynamically, imperfections in crystals are highly energetic and should be eliminated from the perfect crystal structures. Small size makes such elimination
of imperfections possible. In addition, some imperfections in bulk materials, such as dislocations are often created to stresses generated in the synthesis and processing of bulk materials due to temperature gradient and other inhomogeneities. Such stresses are unlikely to exit in small structures, particularly in nanomaterials.

1.6 Synthesis of ZnS nanoparticles by various routes using bottom up approach

1. All reagents were analytically pure and used without further purification. After ZnAc$_2$2H$_2$O (0.005 mol) and Na$_2$S.9H$_2$O (0.005 mol) were put into a round-bottom glass flask of 50 ml containing 20 ml EG, the flask was immediately placed in a microwave oven (650 W, 2.45 GHz) irradiating for 10 min with the power of 10% (65 W). Then, the system was allowed to cool naturally to room temperature and a white precipitate was obtained. The precipitate was washed with distilled water and ethanol several times to clear out NaAc and EG and then dried in air at 50°C \[80\].

2. A piece of grafted polypropylene membrane (10 mm x 10 mm) was first immersed into 50 ml 0.2 mol L$^{-1}$ ZnSO$_4$ aqueous solution under stirring. After 30 min, the grafted membrane complexed with Zn$^{2+}$ was taken out and washed by distilled water. The membrane was then dipped into 50 ml 0.2 mol L$^{-1}$ Na$_2$S aqueous solution under stirring for 30 min and washed again with distilled water thoroughly and then dried in a vacuum oven at 80°C for 8 h and weighed. Weight increase of the sample was calculated from the weight change before and after treatment by the ZnSO$_4$ and Na$_2$S aqueous solutions \[81\].

3. In a typical hydrothermal synthesis experiment analar grade Zn(NO$_3$)$_2$·6H$_2$O (0.04 moles) and thiourea (0.04 moles) are dissolved in 200 ml of deionized water and the solution was transferred to autoclave SS pressure vessel. The autoclave was programmed to reach 170°C in 1 h (ramp time) and at this temperature the reaction was kept for 2 h (soak time) with stirring speed of 400 rpm. During the experiment the in situ pressure developed was 15 atm. When autoclave temperature reached to RT, the solution with precipitate
(pH~8) was filtered and washed with distilled water to get neutral pH. The white filtered solid was dried overnight in oven at 120°C [82].

4. Nanoparticles of ZnS are synthesized as free standing powder by wet chemical synthesis method with the use of Na₂S instead of thiourea as sulfur source. NH₃ solution (10 M) is slowly added to 20 ml of 1 M ZnCl₂ in a 100 ml beaker with stirring. NH₃ solution is then added until the white precipitate formed completely dissolved. Two milliliter of 1 M TEA, which is the capping agent, is then added. To this solution, 30 ml of 1 M Na₂S is added drop wise while the reactants are continuously stirred. The white precipitate formed is centrifuged, washed several times with water and finally with acetone, and then air dried to obtain nanopowders of ZnS [83].

5. A synthetic inverse miceller methodology used to prepare ZnS and nanoparticles. Nanoparticles were synthesized in water-in oil inverse micellar assemblies (W=2), prepared with Zn(CH₃-COO)₂ (4.5 mL of 0.15 M aqueous solutions) plus AOT , n-heptane and Na₂S as sulphur source . The resultant nanoparticles were capped by reaction of 0.72 mL of 4-fluorobenzenethiol and 0.9 mL of triethylamine and dispersed in 20 mL of acetone to form sols of 4-fluorophenylthiolate-capped ZnS nanoparticles. Gelation, aging, and drying to yield xerogels of ZnS [84].

6. Wurtzite-structure ZnS nanobelts were synthesized by a solid–vapour phase thermal-sublimation technique. These ZnS nanobelts were synthesized by heating bulk ZnS in flowing argon with the assistance of Au particles acting as catalyst [85]. The resulting ZnS nanobelts were deposited on an alumina substrate then they were removed from the substrate and loaded without any preparation for various characterization [86].

7. All synthesis was carried out in water for its inherent advantages of being simple and environment friendly. All steps of the synthesis were performed at room temperature and under ambient conditions. Ten grams of sodium polyphosphate namely SHMP (Fluka Chemika) and STTP (Fluka Chemika) were separately dissolved in 70 cm³ of De-ionized (DI) water and stirred. To each of this an aqueous solution of 0.25 M Zn(CH₃-COO)₂ (Univar) and 1mM Mn(CH₃-COO)₂ (Fluka Chemika) was mixed together and stirred constantly and heated till boiling. After cooling to room temperature, 0.25 M sodium sulfide (Panreac) was added drop wise in an ice bath with constant
stirring, resulting in formation of white precipitate of ZnS nanoparticles almost immediately. The supernatant was then centrifuged at 4000 rpm for 20 min to separate undesired agglomerates. In a few of the experiments, after washing the particles with de-ionized water the sample was freeze-dried to obtain fine powder of ZnS:Mn\(^{2+}\) nanoparticles [87].

8. For preparing nanocrystal of ZnS, the matrix of polyvinyl alcohol (PVA) is prepared by stirring for 3 h with temperature controlled magnetic stirrer. The matrix is mixed with the reactants zinc chloride (ZnCl\(_2\)) solution and then again stirred. As soon as the nanostructure is formed it immediately enters into the gap and can neither come out nor can enhance in size. The particle size is controlled by varying temperature of the reaction, amount of reactant, stirring rate, and pH of the solution. The film over glass substrate contains the nanocrystalline of ZnS specimen embedded in PVA matrix [88].

9. For Electrochemical properties of ZnS/C composite as an anode material for lithium ion batteries ZnS nanoparticles were prepared by a precipitation method using Na\(_2\)S·9H\(_2\)O and ZnCl\(_2\)·4H\(_2\)O as reagents. In a typical procedure, the hydrate solution of zinc chloride was added in the sodium sulphide hydrate solution drop by drop with slow stirring at room temperature, and then stirred continuously at 60 °C for 2 h to form white precipitate. The resulting white precipitate was cooled down and filtered and washed with de-ionized water, and dried at 80 °C to obtain the dried ZnS precipitate. The dried ZnS precipitate mixed with citric acid (CA) uniformly and then calcinated under argon at 700 °C for 90 min to obtain the ZnS/C composites [89].

10. Samples of different sized nanoparticles have been prepared by chemical method using zinc chloride and thiourea. ZnCl\(_2\) was dissolved in distilled water with different molar concentration and so obtained molar solution was stirred continuously for 20 minutes. H\(_2\)S produced by heating the thiourea is then passed through the stirred solution. The white precipitate of the ZnS nanoparticles is formed slowly in the solution. The obtained precipitate was then filtered and dried at room temperature. After sufficient drying, the precipitate was crushed to fine powder with the help of mortar and pestle for further characterization [90].
11. Mn$^{2+}$ doped ZnS nanoparticles were formed by precipitation with H$_2$S gas from a precursor solution containing 0.01 M Zn(CH$_3$COO)$_2$ in the presence of hydroxypropyl cellulose (HPC) as a stabilizer. Doping of Mn$^{2+}$ ions into ZnS nanoparticles was realized in situ during the precipitation procedure. The Mn concentration was chosen as 2 mol % with respect to the cations. After dip coating and drying at 423 K on sodalime glass substrates, the sheets were transparent and colorless and had thicknesses of up to 50µm [91].

12. All the reagents used in our experiment were of analytical purity and were used without further purification. An appropriate amount of zinc chloride (0.1 M), sulphur powder (0.1 M), NaOH (5 M) and deionised water (100 mL) were refluxed together for 5 h under constant stirring. Upon reflux, the product was centrifuged and washed several times with deionised water. The sample was then dried in the oven at 80°C for 2 h to obtain powders of ZnS nanoparticles which appear white in colour [92].

13. Aqueous micellar solution of Sodium Dodecylsulphate (SDS) at 10 mM (cmc~8 mM) in doubly distilled water was prepared. 0.05 M aqueous Zn(OAc)$_2$ solution was then added with a Hamilton microsyringe into 5 ml of the SDS solution and the components were thoroughly mixed. Freshly prepared 0.05 M Na$_2$S solution was then added into the solution in the ratio Zn(OAc)$_2$ : Na$_2$S = 1 : 2 (v/v). The ZnS nano crystals formed in the micellar medium were gray in color. The concentration of the Zn(OAc)$_2$ in the experimental solutions was varied in the range of 50 to 500 µM [93].

14. For synthesis of L-cysteine-capped nano-ZnS L-Cysteine (1.9701 g) was added to 50 mL of thoroughly degassed, vigorously stirred, and N$_2$-saturated 1 mol L$^{-1}$Tris buffer. A 6.25mL aliquot of ZnS$_{0.4}$ (1 mol L$^{-1}$containing 0.01 mol L$^{-1}$HCl) was added to the solution, resulting in an L-cysteine-to-zinc molar ratio of 2:1. Then, 25.0 mL of 0.4 mol L$^{-1}$ Na$_2$S·9 H$_2$O was slowly added drop wise into the vortex of the solution to afford an S/Zn molar ratio of 2:1. The mixed solution was stirred for 30 min. Finally, the colloidal solution was sealed and incubated for 1 h at 47°C (bath water temperature), followed by 10 min of flushing with N$_2$ to remove most of the unreacted sulfide. The purified functionalized nanoparticles [94], which are soluble,
were used to prepare 1 mol L\(^{-1}\) stock solution. On the day of analysis, this was diluted with water as needed [95].

15. An aqueous solution of 0×15 M ZnCl\(_2\) and 0×0045 M MnCl\(_2\) was made such that the molar ratio of Mn to Zn was 3 : 100. The aqueous solution was mixed into as prepared 2×5 wt.% transparent polyvinyl alcohol (PVOH) matrix under ~ 200 rpm stirring condition. Temperature was maintained to 65°C. Into this, dropwise injection of Na\(_2\)S solution led to growth of ZnS quantum particles in PVOH matrix. Also, the ZnS nanoparticles are synthesized by grinding as received ZnS powder (99% pure, Lab Chem) mechanically, followed by sintering (~ 900°C) and finally quenching into ice-cold PVOH matrix. Colourless or faint milky coloured Mn doped ZnS samples were developed on the laboratory glass slides [96].

16. Synthesis of ZnS nanoparticles, having two different average sizes, were carried out using a chemical route. In this case aqueous solutions of zinc chloride (ZnCl\(_2\)) and anhydrous sodium sulphide (Na\(_2\)S) were reacted in the presence of thioglycerol or TG[HSCH\(_2\)CH(OH)CH\(_2\)OH]. Synthesis was carried out at room temperature. ZnCl\(_2\) and TG were mixed in a reaction vessel and stirred continuously under nitrogen atmosphere. Na\(_2\)S was added drop-wise to the solution. After the reaction was completed the solution was stirred for sometime and then air-dried to get nanoparticles in the form of a white precipitate. The precipitate was thoroughly washed with water and air dried to obtain ZnS nanoparticles for the analysis. By varying the molarity of capping agent viz. TG, samples with different average sizes could be produced [97].

17. Synthesis of ZnS nanoparticles by gas evaporation technique was performed by AC arc-discharge evaporation. When the electric current passed through electrodes A and B in the sample preparation chamber the temperature of contact point of electrodes A and B became extremely high and carbon vapor can be produced at the contact point. Since the smoke of carbon rose at the contact part of two electrodes, the convention flow stated at the point of contact. ZnS powders that had been placed at various locations on the tip of electrode A were evaporated together with carbon. Various locations were selected for the evaporant, because the smoke particles can be obtained at about 1 Torr vapor pressure at the evaporation positions. Since the smoke of
carbon rose at the contact part of two electrodes, the convection flow started at the point of contact. The plate set immediately above the carbon electrode was used as the guide plate in order to guide the flow of the evaporated ZnS vapor to the convection flow of carbon. By this method, very low melting point materials can be mixed with carbon in the vapor phase [98].

18. For the purpose of green synthesis of ZnS nanoparticles Zn (NO$_3$)$_2$(1M) solution, Na$_2$S (1M) solution is added drop wise with continuous stirring. A white coloured solution is formed which is further shaken on a magnetic stirrer for 15 hours. Now, 1.0 M glucose solution is added drop wise in this white coloured solution. The resultant solution is heated and incubated at 700°C for more than 6 hours. Precipitates obtained are centrifuged with 2,000 rpm for 15 mints. The final product is dried at 50°C for 4 hours and then crushed to fine powder [99].

19. Nanoparticles of Cu doped ZnS (Zn$_{1-x}$Cu$_x$S where x=0.00, 0.03, 0.05, and 0.10) were prepared by the chemical precipitation method. Freshly prepared aqueous solutions of chemicals were used for the synthesis of nanoparticles. 0.1M zinccsulfate, 0.1M copper sulfate and 0.1M sodium sulfide were used as reactant materials. Freshly prepared 50ml of aqueous solution of 0.1M sodium sulfide was mixed drop by drop in 50 ml of 0.1 M solution of zinc sulfate and 50 ml of 0.1 M solution of copper sulfate using vigorous stirring and then added 0.05g of polyethylene glycol as a capping agent. After the completion of reaction, the solution was allowed to settle for some times and the supernatant solution was then discarded carefully. The remaining solution was filtered and washed several times with distilled water. The wet precipitate was dried in an oven at 80 °C for 2h and then calcined at 100°C for 30 min with a heating rate of about 10°C/min in a muffle furnace [100].

1.7 Applications of ZnS nanostructures

It is worth noting some of the applications that motivated the studies of Zinc Sulfide. Zinc Sulfide has many applications. Rutherford and others first used zinc sulfide in the early years of nuclear physics as a scintillation detector. A scintillation detector measures ionizing radiation. Zinc Sulfide does this because it
emits lights on excitation by x-rays or electron beam. Utilizing this aspect, ZnS is used in x-ray screens and cathode ray tubes [101-103].

Recently, ZnS scintillation detectors have even been used in the potential detection of dark electric matter objects (DAEMONS) [104]. These objects can catalyze the fusion of light nuclei, suggesting new ways for solving the problem of deficiency of solar neutrinos and of solar energetic as a whole. ZnS is also an important phosphor host lattice material used in electroluminescent devices (ELD), because of the band gap large enough to emit visible light without absorption and the efficient transport of high energy electrons. Electroluminescent display devices consist of several layers.

**Figure 1.7** Schematic of an electroluminescent display (ELD) device with ZnS as the phosphor material.

The central layer is a phosphor which emits light when an electric field on the order of 1.5 MV/cm is applied across it. Because of this high field lever, current limiting insulating layers are placed on either side of the phosphor. Finally, electrodes on the top and bottom of the device form the basic capacitive structure. Of course, in order to view the emitted light, at least one of the electrodes must be transparent [105]. This setup is shown in **Figure 1.7** ZnS phosphors are also used in light-emitting diodes (LEDs).

1.7.1 **Field-emission applications**

Field emission (FE), as one of the main features of nanostructures, is of great commercial interest in displays and other electronic devices [106]. In case of
highly ordered nanostructure arrays, it not only has an advantage of faster device turn-on time, compactness, and sustainability compared to the conventional bulky technologies, but aligned nanostructures with a high packing density can significantly enhance the FE properties of materials [107–109].

As discussed in two previous reviews [106,110] the turn on field, threshold field, field enhancement factor, FE current density, and its stability are the key parameters of one material FE performances. These properties are strongly dependent on the work function of an emitter surface, the radius of curvature of the emitter apex, the emission area, the aspect ratio and arrangement style of the emitter, etc. Analyzing all the FE results on ZnS nanostructures, it has been demonstrated three facile routes have been developed to optimize the FE performances of ZnS nanostructures, namely can be enhanced through (i) increasing its aspect ratio (length to thickness ratio), [111] (ii) synthesizing a sharp-tip nanostructure, [112] and (iii) assembling it into arrays [113].

FE measurements show that these crystal orientation-ordered ZnS nanobelt quasi-arrays are decent field emitters although the work function of ZnS (~7.0 eV) is larger than that for some other popular inorganic semiconductor field-emission materials [106].

1.7.2 Room-Temperature UV Lasing

A laser, which is an acronym for Light Amplification by Stimulated Emission of Radiation, is a device that converts energy into light with a mechanism for emitting electromagnetic radiation via a process of stimulated emission. Room temperature semiconductor lasers are attractive for the opto-electronic applications, such as optical communications and other lightwave technologies. Early double heterostructure lasers in GaP-GaAs system fabricated by vapor phase epitaxy (VPE) occur only at liquid nitrogen temperature, similarly to homojunction lasers, owing to lattice mismatch [114].

A continuous wave (CW) operation of semiconductor lasers at room temperature was achieved in the early 1970s [115]. The realization of semiconductor lasers emitting short wavelength UV light is of considerable interest for a wide range of
applications including optical computing, high-density data storage and material processing, and chemical/biochemical microanalysis [116–118]. The achievements of room temperature greenblue diode laser structures with ZnSe, GaN, SiC and In$_x$Ga$_{1-x}$N as the active layers promoted significantly the development of short-wavelength semiconductor lasers [119-122].

However, almost all the researches focused on zero-dimensional (0D) and two dimensional (2D) structures, especially on their thin film and multi-quantum-well (MQW) structures. In 2001, Yang and co-workers demonstrated the first room-temperature ultraviolet lasing in semiconductor ZnO nanowire arrays [117].

They realized that the ZnO hexagonal nanowires bear striking similarities to the conventional macroscopic laser cavity. This discovery led to a flurry of researches into photonic properties of 1D nanostructure. ZnS is a wide bandgap (\(~3.72 \text{ eV and } \sim 3.77 \text{ eV}\) for cubic ZB and hexagonal WZ ZnS, respectively) compound semiconductor that is suitable for a sub-wavelength laser cavity in the UV region (below 400 nm). Moreover, the binding energy of the exciton for ZnS is about 39 meV, which is much greater than the thermal energy at room temperature of 26 meV, making ZnS become an ideal candidate for efficient excitonic laser action at room temperature. Subsequently, they discovered the similar room temperature UV lasing from the homoepitaxial growth of ZnS nanowires and nanoribbons on the surfaces of micrometer-wide single-crystal ZnS nanoribbon substrates [123].

### 1.7.3 Visible-Blind UV-Light Sensors

In recent years, the use of nanostructured materials with tailored geometry as building blocks of functional devices including chemical/biological/gas sensors and photodetectors has attracted intense attention due to their high surface to-volume ratio and its rationally designed surface [124-126]. The electrical integration of chemically synthesized 1D nanostructures has been achieved with lithography, optical integration, which promises high speeds and greater device versatility [127]. The interest in developing high-performance photodetectors has culminated in the realization of individual nanowire/nanobelt photodetectors with ultrafast recovery speed and ultrahigh quantum-efficiency [128-131].
Visible-blind UV-light sensors measure the power or intensity of incident UV radiation while it is blind or insensitive to visible light. Such sensors are very likely to be used in our daily life since prolonged exposure to UV radiation is one of the main reasons to cause skin cancer. In 2009, researchers have successfully assembled individual ZnS nanobelts into devices using optical lithography with the assistance of a pre-designed mask and electron beam deposition, [132] with its uncovered part exposed to the incident light. The optoelectronic measurements show the individual ZnS nanobelt-based sensor is extremely sensitive to UV light exposure (320 nm, over 3 orders of magnitude upon the illumination) while the dark current of the device is below the detection limit (10 \(-14\)A) of the current meter. The photocurrent increase allows us to reversibly switch the device between “UV ON” and “UV OFF” states.

1.7.4 Nanogenerator for Electricity Generation

Electricity generation is the process of creating electricity from other forms of energy. The unique properties of nanostructures associated with their low dimensionality give rise to new opportunities for research on energy conversion, and especially semiconductor nanostructure arrays provide a novel route to advance solid-state energy conversion and storage devices [133-134].

This discovery of nanogenerator on ZnO nanowire arrays is not by accident, but due to the unique coupling of piezoelectric and semiconducting properties of ZnO and the formation of a Schottky barrier between the metal and ZnO contacts. Although the output power and voltage are still weak to power our homes lights, this nanogenerator is able to power battery-free wireless nanodevices by converting ambient vibrations, hydraulic energy, or mechanical movement to electricity. Similar with ZnO, ZnS exhibits both semiconducting and piezoelectric properties that can form the basis for electromechanically coupled sensors and transducers. Wang and co-workers demonstrated ZnS nanowire arrays the potential to be used for piezoelectric energy generation that it is able to convert mechanical energy into electricity when they are deflected by a conductive AFM tip in contact mode. However, the output signal for ZnS nanowire arrays is lower than that for ZnO nanowire arrays [135]. A literature survey on various application of ZnS nanostructure in listed in Table 1.4.
# Table 1.4 A summary on the ZnS nanostructure arrays and their application

<table>
<thead>
<tr>
<th>Nanostructure</th>
<th>Synthesis method Reported</th>
<th>Growth temp (°C)</th>
<th>Grown substrate</th>
<th>Property/Application</th>
<th>Ref.</th>
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<tr>
<td>Nanowire arrays</td>
<td>Template-assisted VLS growth process</td>
<td>1100</td>
<td>Within ordered channel AAM</td>
<td>Optical properties, PL, and room temperature UV lasing</td>
<td>[136]</td>
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<td>Template-assisted electro deposition</td>
<td>120</td>
<td>Within ordered channel AAM</td>
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<td>Heteroepitaxial growth</td>
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<td>CdS nanoribbon substrate</td>
<td>Optical properties, CL, and room temperature UV lasing</td>
<td>[138]</td>
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<td>A facile evaporation condensation approach</td>
<td>1050</td>
<td>Si wafer</td>
<td>Field-emission</td>
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<td></td>
<td>A simple thermal evaporation route</td>
<td>Within 400 to 500</td>
<td>Zn foil</td>
<td>Optical properties, PL and Field emission</td>
<td>[140]</td>
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<td>One-step solvothermal method</td>
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<td>Zn substrate</td>
<td>Optical properties, PL and Field emission</td>
<td>[141]</td>
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<td>1050</td>
<td>Highly conductive Cu substrate</td>
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<td>Selective etching of ZnO-ZnS nanowire arrays</td>
<td>1100 for the synthesis of ZnO-ZnS and RT for etching</td>
<td>ZnS buffer layers</td>
<td>Optical properties, CL and electricity generation</td>
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<td>650</td>
<td>c-plane Al₂O₃ substrate</td>
<td>Optical properties PL</td>
<td>[143]</td>
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<td>ZnO thin film</td>
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<td>An aqua-sol hydrothermal process</td>
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<td>Pulse-plating Zn nanocrystallines</td>
<td>——</td>
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<td>Grown substrate</td>
<td>Property/Application</td>
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<td>One-step, wet-chemical approach</td>
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<td>[149]</td>
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<td>ZnS sheet</td>
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<td>A simple solvothermal reaction and subsequent heat treatment</td>
<td>250</td>
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<td>Field-emission</td>
<td>[151]</td>
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<td>A simple solvothermal reaction and subsequent heat treatment</td>
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<td>Field-emission</td>
<td>[152]</td>
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<td>Zn foil</td>
<td>Optical properties, CL</td>
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<td>Single-crystal ZnS nanoribbon substrate</td>
<td>Optical properties, PL and CL, and room temperature UV lasing</td>
<td>[123]</td>
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<td><strong>Horizontal Nanobelt arrays</strong></td>
<td>A simple CVD growth process</td>
<td>1100</td>
<td>A predesigned patterned substrate (Si covered SiO₂)</td>
<td>Optical properties, CL and UV-light sensor</td>
<td>[132]</td>
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<td></td>
<td>A simple CVD growth process</td>
<td>1050</td>
<td>Si wafer</td>
<td>UV-light sensor</td>
<td>[153]</td>
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</table>
Compare to other methods, the microwave irradiation method is very fast technique to produce uniform size nanoparticles with high purity owing to its short reaction time. It is found that this method is non toxic route to produce ZnS nanoparticles. Looking towards the synthesis of nanoparticles by chemical route, molarity of the solution used, makes great impact on the properties of prepared nanostructures. Keeping that point in mind the molarity variation of the precursors used for the synthesis of ZnS nanoparticles is carried out in the present work.

The narrow-gap-semiconductor Bi$_2$Se$_3$ ($E_g = 0.3$ eV) and its alloys are considered to be the prime candidate for the best room temperature bulk thermoelectric materials found to date [154].

The bonding between Bi-Se is predominantly covalent in character, while between Se-Se is of weak Van der Waals type [155] with Figure of merit (ZT) about 1 at room temperature [156]. Looking to this aspect, we have grown single crystals of Bi$_2$Se$_3$ by vapour phase technique. But if we look at the literature most researchers have grown this crystal by Bridgman technique. Henceforth, this study on transport properties will provide a unique literature not available uptil now on Bi$_2$Se$_3$ single crystals grown by vapour phase technique.

The main objectives of thesis proposed are as follows:

1. Microwave assisted synthesis of ZnS nanoparticles.
2. Molarity variation on synthesis of particles and analysis of its effect on their size.
3. Synthesis of ZnS nanoparticles using different precursors for Zn and S and optimizing its effect on size of ZnS nanoparticle.
4. Characterizing synthesized ZnS nanoparticles by various techniques.
5. Growth of Bi$_2$Se$_3$ single crystal by vapour phase technique and characterize it structurally, electrically and thermally so as to show its utility as thermoelectric material.
1.8. References


[48] X Fang, T Zhaib, U K Gautamb, L Lib, L Wua, Y Bandob, D Golberg, Prog. in Mat. Sci., 56, 175, (2011)


