Chapter 1

Introduction
1. Introduction

Diluted magnetic semiconductors (DMS) have been studied widely during past two decades in view of their intriguing properties [1-2]. DMS bridge the physics of semiconductors and magnetics since they show typical semiconductors behaviour combined with pronounced magnetic properties. Diluted magnetic semiconductor are II-VI, II-V, IV-VI or III-V based semiconducting compounds in which the metal ions are randomly replaced by magnetic ions like Ni, Co, Fe, Mn or rare earth metals [3]. The only fundamental discrete circuit elements that have been left behind are those involving magnetic materials. Semiconductors and magnetic material are very important materials in the current electronic industries. The concept of “magneto electronics” has come up here. DMS are also known as “spintronic” materials as these offer spin as an extra handle to control current in addition to change. Hence these ternary alloys play a vital role in spintronics. DMS materials are present in electronic chips. DMS are expected to play an important role in material science and in future electronics because charge and spin degrees of freedom are accommodated into a single material which exhibits interesting magnetic, magnets-optical, magneto electronics. DMS which combine semiconductor electronic properties with a strong enhancement of spin-dependent phenomena due to the presence of magnetic ions are well-known materials for testing spintronics concepts [4]. An important approach to the development of such new materials is to examine the possibility of magnetizing a functional non-magnetic host by diluted magnetic impurity doping which allows the host to retain its other desirable properties [5]. The corresponding materials are classified as diluted magnetic semiconductors. Considerable success has been achieved in this direction in the domain of III-V and group IV semiconductors [6-8], with some recent success reported in oxide-based systems [9-14]. Unfortunately in the case of many systems, researchers have not yet been able to completely rule out the possibilities of extrinsic effects such as dopant clustering, impurity magnetic phase etc. [15,16] and it has not always been clear that the reported DMS ferromagnetism is indeed included by the carriers. The most relevant feature of DMS, which attracted considerable interest, is the coexistence and interaction of two different electronic subsystems delocalized conduction (s-type) and valence (p-type) band electrons and localized (d or f-type) electrons of magnetic ions . In particular the sp-d exchange interaction leads to strong band splittings, which results in giant magneto optical effects. On the other hand, the d-d exchange interaction coupling randomly distributed
magnetic ions, triggers formation of spin-glass and antiferromagnetic phases depending on magnetic ion concentration and temperature range [17,6]. The great interest in studying the DMS is stimulated by their unique electronic, magnetic and magneto optical properties [13-20].

The present study is focused on CdS-based nano DMS and relevant aspects of DMS and nanomaterials are included in this chapter. The work published on DMS is quite extensive [21-26]. It is not possible to review even briefly. The entire work here, however, in the context of the present study comprises of a few relevant aspects of DMS and nano materials, a review of the earlier work on semiconduction nano particles and on Cd$_{1-x}$Ni$_x$S system in nano-form, followed by the objective and scope of present study.

1.1 Diluted Magnetic Semiconductors

Diluted magnetic semiconductors (DMS) are semiconducting compounds whose lattice comprises substitutional magnetic ions at random. Fig. 1.1 shows the distribution of magnetic ions in a DMS lattice. During the past several years these ternary alloys have attracted a great deal of attention for several reasons. Firstly, the semiconducting properties of DMS, such as the energy gap, the effective mass, etc. can be varied in a controlled fashion by varying the composition, as much as in non-magnetic ternary semiconductors, e.g., Hg$_{1-x}$Cd$_x$Te. Secondly, DMS are of interest for their magnetic properties such as the spin glass transition [27], formation of antiferromagnetic clusters, giant magneto-resistance and other magnetic effects of current interest. Thirdly, the presence of magnetic ions in the DMS lattice leads to spin-spin exchange interaction between the localized magnetic moments and the band electrons. This interaction affects the energy band and impurity level parameters of the semiconductor, (e.g., the electronic g-factors), resulting in new physical effects, particularly when quantizing magnetic fields are present. Such new and potentially important phenomena as the extremely large Faraday rotation in Cd$_{1-x}$Mn$_x$Te giant negative magneto-resistance associated with hopping conduction in Hg$_{1-x}$Mn$_x$Te and the bound magnetic polaron observed in Cd$_{1-x}$Mn$_x$Se are all consequences of the spin-spin exchange interaction [28]. The influence of this magnetic exchange distinguishes DMS from other types of semiconductors. For this reason DMS are also known as semi magnetic semiconductors (SMSC) [20].
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Figure 1.1. General crystal structure of diluted magnetic semiconductors (DMS).

Fig 1.2 represents a DMS lattice. The introduction of the magnetic ion in different semiconductor compounds provides the possibility of using and to study a variety of magnetic and magnetic-optical phenomena not present in conventional nonmagnetic semiconductor. Recently a number of investigations have been focused in the development of new DMS in different semiconductors. Indeed, these investigations have been oriented to find the ferromagnetism at room temperature to realize new classes of spintronic device such as spin valves, transistors, spin light emitting diodes, magnetic sensors, non-volatile memory, logic devices optical isolators and ultra-fast optical switches. The potential advantages of these spintronics devices will be higher speed, greater efficiency, and better stability, in addition to the low energy required to flip a spin.

Figure 1.2. (A) a magnetic semiconductor, in which a periodic array of magnetic element is present, (B) a diluted magnetic semiconductor, an alloy between nonmagnetic semiconductor and magnetic element, and (C) a non-magnetic semiconductor, which contains no magnetic ions.
In the absence of magnetic field DMS with magnetic atoms/ions distributed in a semiconductor lattice substitutionally are ordinary semiconductors but in the presence of magnetic field, significant changes in the band edges and spectacular magneto-optic and magnetic field induced phenomena are observed. The DMS alloys are generally classified into two categories, by virtue of the type of interaction of d' electrons with the band electrons/holes as narrow gap and wide gap diluted magnetic semiconductors. Mercury and lead chalcogenides along with indium based III-V compounds are narrow gap DMS and many of the remaining are wide band gap DMS. Most common DMS are II-VI compounds (like ZnTe, CdTe, ZnSe, CdS etc.) with transitional metal ions (eg. Ni, Mn, Fe, and Co). The exhibition of antiferro/ferromagnetic behaviour critically depends on the specific host and magnetic atoms. In the following sections some relevant aspects of different groups of DMS are presented.

1.2 II-VI DMS

DMS are compound of alloy semiconductors containing a large fabrication of magnetic ions (Mn$^{2+}$, Ni$^{2+}$, Cr$^{3+}$, Fe$^{3+}$, and Co$^{3+}$) that are studied mainly on II-VI based materials such as CdTe and CdS. This is because such +2 magnetic ions are easily incorporated into the host II-VI crystals by replacing group II cations. In such II-VI based DMS such as (CdMn) Se, magneto-optic properties were extensively studied, and optical isolators were recently fabricated using their large faraday effect [29]. Although this phenomenon makes these DMS relatively easy to prepare in bulk form as well as thin epitaxial layers, II-VI based DMS are difficult to dope to create p- and n-type, which makes the material less attractive for applications.

These diluted magnetic semiconductors of A$^{11}_{1-x}$Ni$_x$B$^{VI}$ type are of great interest for several distinct reasons [20].

Their ternary nature gives us the possibility of tuning the lattice constant and band parameters by varying the composition of the material.

The random distribution of magnetic ions over the cation sub-lattices leads to important magnetic effects, e.g., the formation of the spin-glass-like phase at low temperatures.

The substitutional transition metal ions like Ni atoms in the A$^{II}$B$^{VI}$ structure are also characterized by highly efficient electroluminescence, which make dilute magnetic semiconductor alloy important in the context of optical flat panel display applications.
The spin dependent properties lead to dramatic effects, such as the giant Faraday rotation, the magnetic field induced metal-insulator transition, and the formation of bound magnetic polarons.

Due to the tunability of their lattice parameter and their energy gaps, the $A'_{1-x}TM_xB^{VI}$ alloy is an excellent candidate for the preparation of quantum well super lattices and other configuration which involve band-gap engineering.

II-VI DMS, Zn$_{1-x}$Ni$_x$Te has attracted special attention due to the highest miscibility of Ni($x=0.86$), electrical neutrality of magnetic atoms maximum spin value ($S=5/2$). The solubility of Ni is minimum in zinc blends Zn$_{1-x}$Ni$_x$S (i.e. $x=0.1$). The highest miscibilities of Ni, Fe, Co and Cr in II-VI compounds are only 0.26, 0.14 and 0.005 [30]. The nearest neighbor exchange integral is smaller but the range of exchange interaction is larger in the narrow gap DMS than in the wide gap DMS materials [31].

1.2.1 II-V DMS

The solubility of Mn, the most widely studied magnetic atoms, in II-V DMS is only 15%. These are characterized by the smallest cation-cation distance of 0.29nm ([Zn$_{1-x}$Mn$_x$)$_3$As$_2$] compared to the minimum 0.38 nm reported in any DMS. Cd$_3$As$_2$, Zn$_3$As$_2$ and Zn$_3$P$_2$ have been successfully alloyed with Mn to form (Cd$_{1-x}$Mn$_x$)$_3$As$_2$ [32-35], (Zn$_{1-x}$Mn$_x$)$_3$As$_2$ [36-39] and Zn$_{1-x}$Mn$_x$P$_2$ [40]. Quaternary (Cd$_{1-x}$Zn$_x$Mn$_3$)$_3$As$_2$ [41-43] and Fe based DMS (Zn$_{1-x}$Fe$_x$)$_3$As$_2$ [44] have also been prepared recently. In CdP$_2$ doped with Mn [45] and CdSb doped Fe [46], contrary to other II-V DMS, Mn replaces the 'V' group atoms i.e., and Sb respectively.

1.2.2 III-V DMS

Miscibility of transition metal ions in III-V host lattices is very low and obtaining equilibrium and optimum growth conditions is much more difficult. Hence III-V based DMS are not studied extensively compared with other DMS using equilibrium growth processes. However, non equilibrium methods like MBE have been used extensively. GaMnAs crystals were obtained with very low concentration of Mn (i.e. $x<0.001$) [47]. Preparation of a new GaMnAs DMS by molecular beam epitaxy was reported [48]. In$_{1-x}$Mn$_x$As epilayers with $x=0.15$ [49-51] and Ga$_{1-x}$Mn$_x$As epilayers with for $x=0.07$ were also successfully grown [52]. A ternary DMS, Ga$_{1-x}$Mn$_x$Sb was grown with different Ni concentrations using Bridgman growth technique [53]. III-V based DMS are used in opto-electronics and spintronics [49-51] and hence there is a need to study II-V DMS with top priority.
1.2.3 IV-VI DMS

IV-VI DMS, a number of interesting effects are observed due to the presence of magnetic ions and their exchange interactions with its inerrant carriers. Carrier concentration induced para/ferro/antiferro/spin-glass formations are some of the interesting effects reported [54-55]. These are effective mid-infrared tunable detectors [56] and can compliment the lasing wavelengths of III-V compounds. Pb-Pb1_xEu_xTe heterostructure work as infrared lasers even at 223K [57]. The magnetic properties of these crystals were found to be carrier independent in contrast to the magnetic properties of Sn1_xMn_xTe crystals [58].

1.3 Properties of II-VI based DMS

Since the present study is on II-VI (CdS) based DMS, some important aspects of II-VI DMS are outlined in the following sections.

1.3.1 Crystal Structure of II-VI DMS

Most of the properties of DMS are strongly dependent on the equilibrium crystal structure of a DMS. The ternary alloys formed by substituting magnetic element for group II element in the $A^{II}B^{VI}$ lattice retain the crystal structure of the "parent" $A^{II}B^{VI}$ compound up to a critical value of the dopant concentration. In their crystal structure, the mechanical, optical and electrical properties of DMS are qualitatively similar to their nonmagnetic "parent" compounds. However, when the concentration of the magnetic element becomes appreciable, the lattice becomes strained and structural transitions become imminent. Most of the II-VI based DMS crystallize in zinc blend structure; although in some both wurtzite and zinc blend structures co-exist. These structures are shown in Fig. 1.3.

![Figure 1.3. Unit cells in the (a) zinc-blende (b) wurtzite structures and (c) Zinc-blende structure of CdS.](image-url)
The crystal structures (zinc blend and wurtzite) of DMS are very closely related inspite of difference in their symmetry. They are formed with tetrahedral (s-p$^3$) bonding, involving the two valence s electrons of the group II element and the six valence p electrons of group VI element. The transitional metals can contribute their 4s$^2$ electrons to the s-p$^3$ hybridization and can substitutionally replace group II elements in tetrahedral structures of II-VI lattice.

1.3.2 Band Structure of II-VI DMS

Parameters like energy gap, lattice parameter, crystal structure etc, are tailorable with the concentration of the dopant magnetic ion in DMS alloys. Fig. 1.4 shows a typical band structure diagram of a wide gap II-VI DMS [20]. The band structure in DMS is essentially same as that of the host lattice except that the d-electron states are split in the presence of crystal field. The ‘d-d’ and ‘sp-d’ exchange interactions determine the bulk magnetization. When magnetic atoms are incorporated, sp-d hybridization broadens the ‘d’ levels into relatively flat and narrow bands. The location of $e_g$ level is about 3.5 eV below the top of the valence band [59-61]. This value is the same for all Mn doped II-VI alloys. Qualitatively the band diagram of narrow gap DMS is similar to that of wide gap DMS. But the band structure of the host is not similar and shows band inversion at some composition of the magnetic atoms leading to zero band gap. In some DMS (Hg$_{1-x}$MnxTe), the band gap variation with composition is very much higher compared to their non-magnetic counterpart Hg$_{1-x}$Cd$_x$Te [62]. Effective mass and the large spin splitting factor considerably increase the cyclotron splitting. These splitting energies are appreciable and hence no longer can be neglected. Fig. 1.5 shows the spin splitting of conduction and valence bands for wide gap DMS in the presence of magnetic field. In the absence of magnetic field such split in energy levels will not affect the properties of the DMS. However, an applied magnetic field brings about dramatic changes.

The energy gap does not vary linearly with composition in most of the DMS systems i.e., there is some deviation (bowing) from linearity. The degree of deviation from linearity is normally described by a parameter called ‘bowing parameter’. In some alloy systems, the energy gaps of some intermediate compositions are found to be even less than the values of the end compound [63-64]. Pseudopotential [65]/dielectric [66] models explain the bowing in energy gaps of alloy systems. Chuu et al [67] attributed the observed bowing in Cd$_{1-x}$MnxS to inter substitutional atoms rather
than to the structure of the lattice itself. Similar bowing in energy gap was reported in other alloy systems also [63, 64, 68, 69]. This phenomenon is called ‘band bowing’.

![Schematic band structure of wide gap zinc blende DMS crystals.](image)

Figure 1.4. Schematic band structure of wide gap zinc blende DMS crystals.

![Band structure near the Γ point for three cases: an open gap Zinc-blende semiconductor, a zero-gap zinc-blende semiconductor and a wurtzite semiconductor.](image)

Figure 1.5. Band structure near the Γ point for three cases: an open gap Zinc-blende semiconductor, a zero-gap zinc-blende semiconductor and a wurtzite semiconductor.

### 1.3.3 Luminescence Properties

The ternary alloys \(A_{1-x}^{III}Ni_xB^{VI}\) are formed by substituting the magnetic transitional ions \(Ni^{2+}\). In these the 3d shell of the \(Ni^{2+}\) ion is only half-filled. This leads to new intra \(Ni^{2+}\) electronic transitions, which dominate the optical properties of the \(A_{1-x}^{III}Ni_xB^{VI}\) alloys at high values of ‘\(x\)’, and are responsible for different coloured photo-emissions. Such emission of light by a material under photo-excitation is called photoluminescence. To understand the intra \(Ni\) transitions a free atom is considered. It has the \(3d^54s^2\) configuration. Five 3d electrons are aligned in the ground state according to Hund’s rule (\(↑↑↑↑↑\)). In this state the Ni atom has a total spin
quantum number $S = 5/2$ and a total angular momentum $L = 0$. The lowest excited states of the atom correspond to $L = 1, 2, 3$ and 4. To make transition to one of these $L \neq 0$ states requires flipping of at least one of the electron spins (\(\uparrow\uparrow\uparrow\uparrow\downarrow\)), i.e. a change to the spin quantum number $S = 3/2$. In spectroscopic notation, the states are identified by the label $^{2S+1}L$. Thus, the ground ($S = 5/2, L = 0$) state of the Ni atom is labeled $^6S$ and the $L = 1, 2, 3$ and 4 excited states corresponding to $S = 3/2$ are $^4P$, $^4D$, $^4F$ and $^4G$, respectively. The transitions indicated in Fig. 1.6 cause the photo and electroluminescences.

![Schematic diagram of the splitting of the lowest excited state of the 3d$^5$ level ($^2G$) relative to the ground state ($^6S$) for a Ni$^{2+}$ ion in the presence of a tetrahedral crystal field.](image)

**Figure 1.6.** Schematic diagram of the splitting of the lowest excited state of the 3d$^5$ level ($^2G$) relative to the ground state ($^6S$) for a Ni$^{2+}$ ion in the presence of a tetrahedral crystal field.

### 1.3.4 Electrical Properties

Electrical properties provide useful information about the concentration and nature of charge carriers, band structure and also various scattering mechanisms of the carriers. In II-VI compounds three interactions are important in scattering of carriers. They are polar optical mode scattering, piezoelectric scattering and impurity scattering. In II-VI compounds, the effective mass of the charge carriers are generally larger and the dielectric constants are smaller than those of Ge and Si. Hence the electrons are more tightly bound in these compounds. In these compounds, the type and concentration of charge carriers cannot be easily measured by external doping due to auto compensation. Phonons, magnons, ferrons, anti-ferrons, drag of phonons and magnons are some of the transport mechanisms. In contrast to ferromagnetic metals,
ferromagnetic semiconductors display a peak in resistivity and a discontinuity in
temperature coefficient of resistivity and specific heat at the Curie temperature.
Paramagnetics are not found to show peak in resistivity in degenerate semiconductors;
but a kink at Neel temperature (T_N) has been reported [21, 22]. Specific heat behavior
is similar to that of ferromagnetic semiconductors. Normally thermoelectric power at
low temperatures arises due to diffusion and phonon drag. In magnetic
semiconductors the magnon drag is shown to be small. In low magnetic fields,
thermoelectric power is shown to increase with field strength [21, 22].

1.3.5 Magnetic Properties

(a) Exchange Interactions in II-VI DMS

In II-VI DMS, two types of interactions need to be considered. The first being
d-d short-range exchange interaction between ‘d’ electrons of randomly distributed
magnetic ions in zinc blende/wurtzite structures. Nearest neighbor (J_NN) and next
nearest neighbor (J_NNN) exchange interactions of ‘d’ electrons are weak and negative,
and hence they induce antiferromagnetism. The second exchange interaction is with
the participation of itinerant electrons/holes. The localized ‘sp’- hybridized electrons/holes interact with the stationary ‘d’ electrons giving rise to sp-d exchange
interaction. The sp-d exchange interaction influences the transport properties like
Faraday rotation, electrical properties, mobility of charge carriers, negative magnetic
resistance and the properties of bound magnetic polarons (BMP), while the d-d
exchange interactions control the static and dynamic properties of DMS. Different
models have been proposed for understanding d-d and sp-d exchange interactions and
J_d is found to be smaller by an order of magnitude than J_sp-d [70]. The exchange
integrals have been reported from different experiments like high field magnetization
[71-73], neutron scattering [74-76], Raman scattering [77] and susceptibility
measurements [78].

(i) d-d Exchange Interaction

Larsen et al [70] calculated J_dd using perturbation technique and showed that it
has three contributions arising from superexchange, the Bloembergen-Rowland
mechanism and Ruderman-Kittel-Kasuya-Yosida (RKKY) like process between
conduction electrons. The dominant contribution arises from the hybridization
induced superexchange involving only anion derived upper valence band states and
the Ni ‘d’ states. This is also the dominant mechanism in narrow gap DMS where
Bloembergen-Rowland interaction is supposed to contribute significantly [79]. A paramagnitised super exchange integral in terms of band parameters is given by

\[ J^{\text{dd}}(R) = -2 (V_{dd}) \left( (e^{g^*}_d + U_{\text{eff}} - E_v)^3 + (e^{g^*}_d + U_{\text{eff}} - E_v)^3 \right) f(R) \] (1.1)

where \( f(R) \) is the radial distribution function and \( U_{\text{eff}}, e^{g^*}_d, V_{pd} \) are the band parameters. Cobalt (Co) based DMS are shown to have substitutionally higher values of \( J_{dd} \) (-47 K to -54 K) compared to the value of Mn based II-VI DMS (-6.3 K to -16.1 K) [80].

(ii) Sp-d Exchange Interaction

Sp-d exchange interaction is described by \( \alpha \) and \( \beta \) superexchange constants arising from the electron and hole interactions with 'd' electrons respectively at the center of the Brillouin zone. \( \alpha \) and \( \beta \) are ferromagnetic and antiferromagnetic ordering. For II-VI DMS \( \beta \) is significantly larger and hence these are antiferromagnetic semiconductors. However, for some Cr based II-VI DMS, \( \alpha \) is high and hence they are ferromagnetic [81-84] semiconductors. \( \beta \) is related to band structure parameters.

\[ N_0 \beta = -32 (V_{pd})^2 \left[ (e^{g^*}_d + U_{\text{eff}} - E_v)^3 + (e^{g^*}_d + U_{\text{eff}} - E_v)^3 \right] \] (1.2)

The energies of Landau levels with spin up and spin down are given by

\[ E_k = E_g + (1+1/2) |h| \omega_c \pm \frac{1}{2} g_{\text{eff}} \mu_B H \] (1.3)

where \( N_0 \) is number of unit cells per unit volume, \( E_g \) is energy gap, \( \omega_c \) cyclotron frequency, \( \mu_B \) is Bohr magneton, \( U_{\text{eff}} \) is polarity energy (-7 eV) associated with addition of an extra electron to a neutral Mn atom in the solid, \( H \) is magnetic field and \( g_{\text{eff}} \) is effective \( g \) - factor which contributes from the usual \( g^* \) factor if electrons determined by band structure as well as from sp-d exchange interaction. This can be expressed as,

\[ g_{\text{eff}} = g^* + \alpha M/(g_{\text{Ni}} \mu_B^2 H) \] (1.4)

\( g^* \) is the band \( g \) - factor and is of the order unity and \( g_{\text{Ni}} \) is the \( g \) - factor of Ni ions and \( M \) is the magnetization. The modified \( g \) factor \( g_{\text{eff}} \), in certain situations like low temperatures and for some specific compositions, attains a very large value [85-88] and leads to unusual effects like large Zeeman splitting of absorption edge negative magneto resistance [89-92], metal insulator transition [93] and formation of bound magnetic polaron [94].
(b) The spin Glass Phase

The spin-glass phase transition of DMS is observed at low temperatures. This conclusion is based on the characteristic cusp exhibited by the low-field magnetic susceptibility at some temperature $T_F$. The low temperature phase is a disordered phase, but "frozen" state, such as a spin-glass phase. For a diluted magnetic fcc lattice with nearest-neighbor interactions only, a spin glass transition becomes possible when magnetic ion concentration exceeds a percolation threshold of $x \approx 0.19$ [95-96]. The spin-glass phase can form for arbitrarily small 'x' at low temperatures.

(c) Giant Faraday Rotation

The ternary alloys ($A^{II}_{1-x}Ni_xB^{VI}$) of the band electrons interact via a strong spin exchange, with the localized 3d electrons of the Ni$^{2+}$ ions, giving rise to large Zeman splittings of the energy bands. These splittings are responsible for giant negative magneto-resistance, enhanced electronic ‘g’ factors and large faraday rotations [31, 97, 98].

The exceedingly large g-factors of the conduction and valence bands lead, in the presence of a magnetic field, to a large Zeeman splitting of the absorption edge; i.e., the energy gap for light of one circular polarization is shifted relative to that for the opposite polarization. A similar large splitting is observed for exciton levels in DMS. This is particularly striking in wide-gap DMS (e.g. Cd$_{1-x}$Mn$_x$Te) [99], because in non-magnetic wide-gap semiconductors, Zeeman splitting effects are relatively small.

The difference in dispersion and absorption for light of opposite circular polarization is particularly strong in the immediate vicinity of the band edge and of the exciton level. This feature provides the dispersion mechanism for Faraday rotation, which attains giant values (of the order of 1000 $\theta/\text{cm-KG}$) at liquid helium temperatures. This very large effect finds potential applications both in diagnostic studies as well as in optical devices (modulators, isolators and other non-reciprocal devices).

1.4 Nanostructures/Nanophased Materials/Nanoparticles

Nanophased material/ nanoparticle is a small solid whose physical dimension lies in the approximate range of a few nano meter (nm) but less than about 100 nm. Nanoparticles having size comparable with the characteristic wavelength of charge carriers are called quantum dots (or) ‘q’ particles. Nanophased materials generally include nanocrystalline thin films sintered materials with an ultrafine grain structure
and loosely aggregated nanoparticles. Size reduction affects most of the physical properties (structural, magnetic, optical, dielectric, thermal etc.) due to surface effects and quantum size effects. Owing to the extremely small dimensions, resulting in a large surface to volume ratio, these materials exhibit properties which are fundamentally different from, and often superior to those of their conventional counter parts.

Research over the past several years has revealed that for smaller values of sizes, properties of the materials change dramatically. Thus geometrical structure, chemical bonds, ionization potential, mechanical strength, melting point, magnetic properties are all affected by the particle sizes and some of the size dependent properties are a topic of discussion in different articles on this issue. A point to be noted here is that for each kind of material there is always a "critical size". This critical size is generally in the range of a few nanometer to few hundreds of nanometers. Typically, when the particle diameter is about 1 to 2 nm there are less than 50 atoms, when particle diameter is about 20 nm, the number of atoms would be $\sim 10^4$ and for larger particles it may be about $-10^5$ to $10^6$. When material dimensions are below 20 nm, their dimensions are either comparable to wavelength associated with electron or hole or at least a few tens of their wavelengths. Larger particles up to a few hundreds of nanometers would be still interesting as long as the number of surface atoms is comparable to the number of bulk atoms. Such particles are important due to their surface effects rather than size effect and are of interest especially in catalysis or chemical reactions. At such sizes materials can not be considered either as large molecules or as a periodic solid, i.e., their properties can not be described by any theory for molecules or that for solids.

1.5 Classification of Nanostructured Materials

All nanocrystalline materials are single phase or multiphase polycrystals, the grain size being of the order of 1 to 100 nm at least in one dimension. They may be equated in nature called as three-dimensional (3D) nanostructured or they can consist of a lamellar structure, they will be termed as layered nanostructured (2D nanostructured) or they can be filamentary in nature (1D nanostructured) [100]. Additionally, Siegel [101] considers zero-dimensional atomic clusters and cluster assemblies. Four basic types of nanocrystalline materials are shown in Fig. 1.7.

The magnitudes of length and width are much greater than the thickness in the layered nanocrystals, and the length is substantially larger than width or diameter in
filamentary nanocrystals. The nanocrystalline materials may contain crystalline, quasicrystalline, or amorphous phases and can be metals, ceramics, or composites. Among the above, the maximum attention has been paid to the synthesis, consolidation and characterization of the 3-D nanostructured crystallites followed by the 1D-layered nanostructured ones. While the former are expected to find applications based on their high strength to improved formability and a good combination of soft magnetic properties, the latter are intended for electronic applications. Relatively fewer investigations have been carried out on the 2D-filamentary nanostructured materials and it is only recently that zero-dimensional clusters are being investigated to ‘tailor’ the optical properties.

Figure 1.7. Schematic representation of four basic types of nanocrystalline materials.

1.6 Semiconductors Nanoparticles

Nanocrystalline material are single-or-multi-phased polycrystalline solids with a grain size of a few nanometers (1 nm = 10^{-9} m = 10 \text{ Å}), typically less than 100 nm. Since the grain sizes are so small, a significant volume of the microstructure in nanocrystalline materials is composes of interfaces, mainly grain boundaries, i.e., a large volume fraction of the atoms resides in grain boundaries. Consequently nanocrystalline materials exhibit properties that are significantly different from and often improved over their conventional coarse-grained polycrystalline counterparts [102]. Materials with microstructural features of nanometric dimension are referred to in the literature as nanocrystalline materials (a very generic terms) nanocrystals/nanostructured materials/nanophased materials. Nanocrystalline structures are not really very new. Nanocrystalline phases are detected in the sample of lunar soils. Many conventional catalytic, materials are based on very fine
microstructures. Nanostructure formed chemically under ambient conditions can also be found in natural biological systems from seashells to bone and teeth in the human body. These materials are notable in that they are simultaneously hard, strong and tough. Therefore, a number of investigations have been conducted to mimic nature (biometrics) and also artificially synthesize nanostructured materials and study their properties and behaviour. These investigation have clearly shown that one could engineer (tailor) the properties of nanocrystalline materials through control of microstructural features, more specifically the grain size. Classifications and important aspects of nanomaterials are presented in the following sections.

1.6.1 Classifications of Nanomaterials

Nanocrystalline materials can be classified into three different categories depending on the number of dimensions in which the materials has nanometer modulations. Thus, they can be classified into (a) layered or lamellar structure, (b) filamentary structure, and (c) equiaxed nanostructured materials. A layered or lamellar structure is one dimensional (1D) nanostructure in which the magnitudes of length and width are much greater than thickness that is only a few nanometers in size. One can also visualize a two-dimensional (2D) rod-shaped nanostructure that can be termed filamentary and in this the length is substantially larger than width or diameter, which are of nanometer dimensions. The most common of the nanostructures, however is basically equiaxed (all the three dimensions [3D] nanostructures) [100].

The nanostructured materials may contain crystalline, quasicrystalline, or amorphous phases and can be metals ceramics, polymers, or composites. If the grains are made up of crystals, the material is called nanocrystalline. On the other hand, if they are made up of quasicrystalline or amorphous (glassy) phases, they are termed nanoquasicrystals and nanoglasses, respectively [102]. Gleiter [103] has further classifieds the nanostructured materials according to the composition, morphology, and distribution of the nanocrystalline component.

Table 1.1 shows classification of the three types nanostructures. Among these, maximum research work is conducted on the synthesis consolidation, and characterization of the 3D-nanostructured crystallites followed by the 1D-layered nanostructures. While the former are expected to find the applications based on their high strength, improved formability, and a good combination of soft magnetic
properties, the latter are targeted for electronic applications. Relatively very few investigations have been carried out on the 2D-filamentary nanostructures.

Table 1.1. Classifications of nanocrystalline materials

<table>
<thead>
<tr>
<th>Dimensionality</th>
<th>Designation</th>
<th>Typical method(s) of synthesis</th>
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<tbody>
<tr>
<td>One-dimensional (1D)</td>
<td>Layered (lamellar)</td>
<td>Vapor deposition Electrode position</td>
</tr>
<tr>
<td>Two-dimensional (2D)</td>
<td>Filamentary</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>Three-dimensional (3D)</td>
<td>Crystallites (equiaxed)</td>
<td>Gas condensation Mechanical alloying/milling</td>
</tr>
</tbody>
</table>

1.6.2 Grain Size Determination

Most of the novel properties of nanostructures are due to their extremely small grain sizes. Hence, the grain sizes determination of nanomaterials is of primary importance. Unfortunately, size determination of nanoparticles is a great task before the scientists. Utility of conventional techniques like X-ray diffraction for particle size determination is often questioned when applied to nanoparticles. This is understandable because long range order which is a prerequisite in X-ray diffraction is not satisfied here.

Although techniques like transmission electron microscope (TEM), scanning electron microscope (SEM), should be of use, there are difficulties of proper sample preparation suitable for size determination. As the properties are size-dependent, one should often like to know the size distribution in a synthesized material and obtained as narrow a size distribution as possible. TEM of some CdS nanoparticles obtained by chemical technique. It can be noticed that particles have different shapes even for almost same size. Grain size determination will be discussed in chapters 3 and 4.

1.6.3 Structure of Nanomaterials

Figure 1.8 shows a schematic representation of hard-sphere model of an equiaxed nanocrystalline metal. Two types of atoms can be distinguished: crystal atoms with nearest neighbor configuration corresponding to the lattice and the boundary atoms with a variety of interatomic spacings, differing from boundary to boundary. A nanocrystalline metal contains typically a high number of interfaces (~6 x 10^{15} m^{-3} for a 10 nm-grain size) with random orientation relationship, and consequently, a substantial fraction of the atoms lies in the interfaces. Assuming, for
simplicity, that grains have the shape of spheres or cubes, the volume fraction of nanocrystalline materials associated with the boundaries, $C$, can be calculated as

$$C = 3\Delta/d$$

where $\Delta$ is the average grain boundary thickness and $d$ is the average grain diameter. Thus, the volume fraction of atoms in the grain boundaries can be as much as 50% for 5 nm grains and decrease to about 30% for 10-nm grains and 3% for 100 nm grains. In contrast, for coarse-grained materials with a grain size of $> 1 \mu m$, the volume fraction of atoms in the grain boundaries is negligibly small. From the foregoing, it is clear that nanocrystalline metals can be considered to consist of two structural components – the numerous small crystallites with long-range ordered and different crystallographic orientations consisting of the “crystalline component” and a network of intercrystalline regions, the structure of which differs from region to region; this will be referred to as the “interfacial component”. The interatomic spacings in the interfacial component have a wide distribution and further the average atomic density is considerably less than the crystal density depending on the type of chemical bonding between the atoms. Both these characteristics of the interfacial component (reduced density and wide distribution of interatomic spacings) have been confirmed by experiments like X-ray diffraction, small-angle X-ray scattering, EXAFS (Extended X-ray absorption fine structure), and other techniques.

Thus, it is expected that the properties of nanostructured materials will be influenced by the grain and grain boundaries. The results of the above studies have been interpreted in terms of grain boundary structures that may be random, rather than
possessing either the short-range or long-range order normally found in the grain boundaries of coarse-grained polycrystalline materials.

1.6.4 Morphology of Nanophase Materials

In nanocrystalline single-phase alloys and pure metals, the most important structural parameter is the grain size. The properties of materials are mostly dependent on the grain size and therefore, an accurate determination of the grain size is important. Both direct (imaging) and indirect (scattering) techniques have been employed to determine the grain sizes. Transmission electron microscopy (TEM) techniques (especially, the high-resolution TEM studies) are ideal to directly determine the grain sizes of nanocrystalline materials using the dark-field technique. The width of the Bragg reflection in an X-ray (large-angle) diffraction pattern can provide grain (or crystal, i.e., the size of the coherently diffracting domain) size information after the appropriate corrections (for instrumental and strain effects) are incorporated. The TEM techniques can clearly indicate whether there is a distribution of grain sizes and it is also possible to obtain a grain size histogram by measuring the grain sizes and counting the number of grains. On the other hand, the X-ray diffraction techniques give only the average crystal size and this value depends strongly on which functions is used when averaging over the size distribution. A number of recent studies discuss the techniques for an accurate measurement of grain sizes and applications of X-ray peak shape analysis techniques to nanocrystalline materials [103, 104].

1.6.5 Atomic Structure of the Grains and the Grain Boundaries

The structure of the grains (crystallites) in nanocrystalline materials has been normally accepted to be the same as in coarse-grained materials. Consequently, there have not been many investigations into this aspect. High-resolution TEM experiments have indicated that nanocrystalline materials consist of small crystallites of different crystallographic orientations separated by grain boundaries. Even though not frequently reported, the grains contained a variety of crystalline defects such as dislocations, twin boundaries, multiple twins and stacking faults.

The structure of the grain boundaries has received a lot of attention and has been discussed extensively in the literature, especially to decide whether it is different in the nanocrystalline and coarse-grained materials of the same compositions. The grain boundary structure determines the diffusivity, and consequently the rate of deformation by grain boundary diffusion (Coble creep) and the rates of sintering and
grain growth. The conclusions differ and some believe that the structure is fundamentally different in both the types of materials while others believe that it is the same. The present status of the structure of grains boundaries in nanocrystalline materials can be found in some recent review articles [105-109].

Gleiter and co-workers [102,103] and others [110] studied the structure of nanocrystalline materials using a number of techniques and showed that the grain boundaries in nanocrystalline materials may be random, rather than possessing either the short-range or long-range order normally found in conventional coarse-grained materials. This randomness has been associated with either the local structure of individual boundaries or the structure co-ordination among boundaries [102]. It was also noted that the boundaries in the as-prepared nanocrystalline palladium (Pd) are in a state with lower atomic short-range order than conventional grain boundaries in polycrystalline materials. The grain boundary free energy of as prepared nanocrystalline Pd was also computed to be twice that of the relaxed state.

EXAFS studies also indicated a much larger reduction in the atomic co-ordination numbers than that detected by X-ray studies, supporting the concept of widely disorder grain boundaries in nanocrystalline materials.

1.7. Properties of Nanomaterials

Because of the very fine grain size and consequently high density of interfaces, nanocrystalline materials exhibit a variety of properties that are different and often considerable improved in comparison with those of conventional coarse-grained materials. These include increased strength/hardness, enhanced diffusivity improved ductility/toughness, reduced density, reduced elastic modulus, higher electrical resistivity, increased specific heat, higher co-efficient of thermal expansion, lower thermal conductivity and superior soft magnetic properties. But, it is becoming increasingly clear that the early results on the properties of nanocrystalline materials or not very reliable mainly due to the significant amount of porosity present in those samples. Thus, for example, the room temperature ductility in ceramic samples has not been reproduced. The properties of nanocrystalline materials are summarized and compared them with those of course grained materials in the following sections.

1.7.1 Mechanical Properties

The strength and hardness of the nanocrystalline materials are 4-5 times greater, when compared to the coarse grained materials and the elastic constant of these materials have been found to be reduced by 30% or less. The various results on
the variation of hardness with grain size reveal a fact that at very small grain sizes, the hardness also decreases with a decrease in grain size. The critical grain size at which this reversal takes place is dependent on the material.

1.7.2 Grain Growth

Grain growth is the process by which the mean grain size of an aggregate of crystals increases. Grain growth occurs in polycrystalline materials to decrease the interfacial energy and hence the total energy of the system. Since nanocrystalline materials have a highly disordered large interfacial component (and therefore they are in high-energy state), the driving force for grain growth is high. However, contrary to the expectation, experimental observations suggest that grain growth in nanocrystalline materials, prepared by almost any method, is very small (and almost negligible) up to reasonably high temperatures.

Grain growth studies in nanocrystalline materials are difficult since the grain size cannot be carried out using TEM, DSC, X-ray diffraction and Raman spectroscopy techniques. Grain growth studies in nanocrystalline materials were conducted by observing the grain size in the synthesized materials and observing its change as a function of time at different temperatures, using direct microscopic observations. It has been noted that grain growth starts at a higher temperature in the nanocrystalline sample with smaller grains and it is rapid above a certain temperature and becomes negligible after annealing the sample for longer durations. The kinetics of normal grain growth under isothermal annealing conditions can be represented by the equation [111]

\[ d^2 - d_0^2 = Kt \]  

where, \( d \) is the grain size at time \( t \) and \( d_0 \) is the mean initial grain size (at \( t = 0 \)). \( K \) is a constant. The above equation is obeyed only at temperatures close to the melting point. If \( d >> d_0 \), the above empirical equation takes the form

\[ d = K' t^{1/n} \]  

where, \( K \) is another constant and \( n \) is the grain growth exponent (values ranging between 2 and 3). The activation energy for grain growth, \( Q \) can be calculated from the equation

\[ K' = K_0' \exp \left( -\frac{Q}{RT} \right) \]  

where \( K_0' \) is a pre-exponent constant, \( R \) is the gas constant and \( T \) is the absolute temperature.
1.7.3 Diffusion and Sinterability

Since nanocrystalline materials contain a very large fraction of atoms at the grained boundaries, the numerous interfaces provide a high density of short-circuit diffusion paths. Consequently, they are expected to exhibit an enhanced diffusivity in comparison to single crystals or conventional coarse-grained polycrystalline materials with the same chemical composition [112]. This enhanced diffusivity can have a significant effect on mechanical properties such as creep and super plasticity, ability to efficiently dope nanocrystalline materials with impurities at relatively low temperatures, and synthesis of alloy phases in immiscible metals and at temperature much lower than those usually required for coarse-grained materials.

The measured diffusivities in nanocrystalline copper are about 14-20 orders of magnitude higher than lattice diffusion and about 2-4 orders of magnitude larger than grain boundary diffusion. For example, the measured diffusivity at room temperature is $2.4 \times 10^{-20} \text{ m}^2/\text{s}$ for 8 nm grain sized copper samples compared to $4.8 \times 10^{-24} \text{ m}^2/\text{s}$ for grain boundary diffusion and $4 \times 10^{-40} \text{ m}^2/\text{s}$ for lattice diffusion [113]. Similarly enhanced diffusivities are also observed for solute diffusion in other metals. It may be mentioned in this context, that some investigators [114] ascribe this increased diffusivity to the presence of porosity in the consolidated samples. For example, if the presence of porosity is properly taken into account, the first diffusivity of nanocrystalline materials has been found to be comparable to that of grain boundary diffusivity. The increased solid solubility limits (the solid solubility of Hg in nanocrystalline Cu has been reported to be 17 at.% against an equilibrium value of <1 at.%) [115]. Formation of intermetallic phases (formation of Pd$_3$Bi at 120 °C, a temperature much lower than normally required for coarse-grained materials) [116] and some times new phases, and increased sinterability of nanocrystalline powders.

1.7.4 Thermal Properties

Since nanocrystalline materials contain a large amount of interfacial volume, the coefficient of thermal expansion (CTE) is expected to be high than in a coarse-grained materials. Accordingly, measured value of CTE of nanocrystalline Cu, Pd, Fe-B-Si and Ni-p alloys are almost twice the values for single crystalline [102]. For example, CTE for nanocrystalline (8 nm) Cu obtained by the inert gas condensation techniques has been reported to be $31 \times 10^{-6} \text{ K}^{-1}$ in comparison with $16 \times 10^{-6} \text{ K}^{-1}$ for copper single crystals.
A comparison of the specific heats of different nanocrystalline, coarse-grained polycrystalline, and amorphous materials suggest that, at room temperature, the specific heat in the nanocrystalline state is much higher than that in the coarse-grained materials and even that of the amorphous materials [117]. While most of the investigators [118] reported a non-linear (parabolic) variation of specific heat with temperature, some people have reported a linear variation. It has also been noted that the specific heat increases at a constant temperature is linear with the reciprocal crystal size.

1.7.5 Optical Properties

(a) Band Gap

The simplest experiment to determine the size dependence in semiconductor nanoparticles is to study absorption spectrum of a material as a function of wavelength of incident photons. The photons are absorbed only when their energy is equal or greater than the energy gap of the semiconductor. Therefore, there is a sudden rise in absorption when photon energy is same as energy gap. If the energy gap increases there is a shift in the onset of absorption towards shorter wavelength. One expects a 'blue shift' with absorption in smaller and smaller clusters, which is indicative of increasing band gap. The optical absorption spectra give the size quantization effect as well as the estimation of band gap.

The different energy states available between valence and conduction bands responsible for radiative recombination are provided by photoluminescence spectra. The nanosize quantized particles yield the best external photoluminescence quantum efficiency and luminescence decay time much faster than the corresponding bulk crystals. The luminescent measurements carried out on various nanocrystals show that the efficiency increases with decreasing size of the nanocrystalline particles.

As shown in Fig. 1.9 one expects a 'blue shift' in absorption in smaller and smaller clusters, which is indicative of increasing energy gap. For very small clusters one uses the terminology borrowed from chemistry. Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) instead of top of valence band and bottom of conduction band in case of extended solid. The size dependent optical absorption shows changing colour of a material. For example in CdS, the bulk semiconductor with energy gap of 2.42 eV is orange in colour. As the clusters become smaller and energy gap increases it becomes yellowish. It is quite easy to show by chemical analysis techniques that this yellow material is CdS and
nothing else. Observation of different colours due to CdSe in glass matrix led scientists to think that CdSe nanoparticles of different sizes may have been formed.

The band gap of semiconductors and the optical transparency behavior of materials could be changed by controlling the grain and/or pore size in the nanocrystalline state for small particle sizes. For example, the band gap of CdSe semiconductor could be changed from 3.0 eV for clusters of 1.2-1.5 nm to 2.3 eV for cluster sizes of 3.0-3.5 nm due to quantum confinement effects; the bulk material has a band gap of 1.8 eV [119]. By controlling the pore size in nanocrystalline Y$_2$O$_3$ to be equivalent to the wavelength of light, scattering could be affected and so the material becomes opaque. On the other hand, when the pore size is much smaller than the wavelength of light, scattering does not take place and so the material is fairly transparent [120]. The optical absorption characteristics can also be modified by allowing interaction to occur between the nanosized CdS clusters [121]. The band gap becomes a function of the grain zone showing a 'blue shift' with decrease in particle size.

![Optical absorption spectra for nanoparticles of different sizes.](image)

Figure 1.9. Optical absorption spectra for nanoparticles of different sizes.

(b) **Luminescence Properties**

Luminescence may be defined as emission of light for certain substance, when excited with radiation like X-ray/UV/electrons and mechanicals stress/chemical reaction/electric discharge/thermal heating etc. The emitted radiation from a luminescent material is free from heating effect and hence is also called as 'cold emission'. Different types of luminescence with mechanisms involved are given in Table 1.2. Manganese is a particularly effective activator in a wide variety of host
lattices, when incorporated in amounts ranging from a small trace up to an order of several percent. The emission spectrum of manganese activated phosphors lies in green, yellow or orange spectral regions. Most of the host materials are silicates, phosphates, sulfides, alkali halides and oxides of Ni, Ca, Mn, Zn, Ba.

Photoluminescence occurs when a system is excited to a higher energy level by absorbing a photon, and then spontaneously decays to a lower energy level, emitting a photon in the process. To conserve energy, the emitted photon can not have more energy than the exciting photon, unless two or more excitation photons act in tandem. Intermediate non radiative downward transitions are possible. The electron can also be stored in an intermediate stage for a long time, resulting in delayed luminescence.

Photoluminescence is divided into two types, depending upon the nature of the ground and the excited states. In a singlet excited state, the electron in the higher energy orbital has the opposite spin orientation as the second electron in the lower orbital. These two electrons said to be paired. In triplet state these electrons are unpaired, that is, their spins have the same orientation. Return to the ground state from excited singlet state does not require an electron to change its spin orientation. A change of spin orientation is need not for a triple state to return to the single ground state (Fig 1.10). Fluorescence is the emission which results from the return to the lower orbital of the paired electron. Such transitions are quantum mechanically, "allowed" and the emissive rates are typically near $10^8$ s$^{-1}$. These high emissive rates result in fluorescence lifetimes near $10^8$ s or 10 ns. The life time is the average period of time a fluorophore remains in the excited state. Phosphorescence is the emission which results from transition between the states of different multiplicity, generally a triplet excited state returning to a single ground state. Such transitions are not allowed and the emissive rates slow. Typically phosphorescent lifetimes range from milliseconds to seconds, depending primarily upon the importance of deactivation processes other than emission.
Figure 1.10. Fluorescence and phosphorescence mechanism.

Table 1.2. Various types of luminescence mechanisms.

<table>
<thead>
<tr>
<th></th>
<th>Description</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>a)</td>
<td>Bio-luminescence</td>
<td>Emission of light by living animals and plants.</td>
</tr>
<tr>
<td>c)</td>
<td>Cando-luminescence</td>
<td>Emission of light by mixed oxides in a gas or hydrogen flame.</td>
</tr>
<tr>
<td>d)</td>
<td>Chemi-luminescence</td>
<td>Luminescence occurring during the course of a chemical reaction and consequentive to the absorption of energy the molecules.</td>
</tr>
<tr>
<td>f)</td>
<td>Electro-luminescence</td>
<td>Emission of light due to electric discharge.</td>
</tr>
<tr>
<td>g)</td>
<td>Radio-luminescence</td>
<td>Luminescence resulting from the bombardment of ionizing particles such a electrons/alpha particles/X-rays and gamma rays.</td>
</tr>
<tr>
<td>h)</td>
<td>Thermo-luminescence</td>
<td>Emission applied due to heating of substances. This phenomenon is dependent on previous storage of energy, for instance consecutive to radio active irradiation.</td>
</tr>
<tr>
<td>i)</td>
<td>Tribo-luminescence</td>
<td>Emission of light due to crushing or rubbing of crystals.</td>
</tr>
</tbody>
</table>

1.7.6 Electrical Properties

Because of the increased volume fraction of atoms lying at the grain boundaries, the electrical resistivity of nanocrystalline materials, as affected by grain boundary scattering, is found to be higher than that in the coarse-grained material of
the small chemical composition. It has also been shown that the electrical resistivity of nanocrystalline materials is sensitive not only to the grain boundaries but also other types of imperfections and/or stresses introduced by the synthesis process [122]. At a constant temperature, the electrical resistivity increases with a decrease in grain size and for a constant grain size, the electrical resistivity increases with temperature, and both these observations are consistent with the theoretical analysis of scattering of electrons by grain boundaries.

The magnitude of the electrical resistivity (and hence conductivity) in nanocomposites can be changed by altering the grain size of the electrically conducting component. For example, by changing the volume fraction of iron particles in a nanocrystalline iron-silica system, the electrical conductivity could be changed by several orders of magnitude.

It has been recently reported that pure nanocrystalline ZnO with 60 nm grain size can exhibit varistor behavior (constant voltage over a wide range of current) with a small, but usable threshold voltage of 0.1 kV/cm [123]. Further, by doping 3–10 nm ZnO with elements like B, Bi, Co, Cu, Sb, and Sn the varistor active range could be extended to 30 kV/cm [124], affording a means of controlling the voltages between 0.1 and 30 kV/cm by choosing the appropriate dopant.

The phenomenon of giant magneto resistance (GMR) drastic decrease of electrical resistivity of materials when exposed to a magnetic field – has been reported in a number of nanocrystalline multilayer and equiaxed systems [125]. Whereas the resistance drop is of the order of 1–2% in conventional materials, the drop in nanocrystalline materials could be as much as 50% or more. Nanostructure materials should be important in magnetic recording applications as new materials are developed with a stable, large GMR effect at room temperature that can operate at magnetic fields as low as a few mT.

### 1.7.7 Magnetic Properties

It is found that the changes in the interatomic distances have a strong influence on the magnetic properties. The saturation magnetization and curie transition temperature of nanocrystalline materials are considerably varied with respect to the bulk materials. Nanocomposites offer another magnetic property, known as magnetocaloric effect i.e., when a material containing small magnetic particulates in a non-magnetic or weakly magnetic matrix is placed in a magnetic field; the magnetic
spins of the particulates tend to align with the field. This increase in magnetic order lowers the magnetic entropy of the spin system.

The coercivity of fine particles increases as the particle size is reduced. The increase in coercivity attains a maximum and then tends to zero. In certain solid solutions, there may be small clusters containing more than the average number of magnetic ions, surrounded by non-magnetic ions. These magnetic clusters within the solid solution then act superparamagnetically [126].

1.7.8 Chemical Properties

The corrosion behavior of nanocrystalline nickel-based alloys has been reported [122]. As expected, the average dissolution rate of Ni was found to be higher than that for the coarse-grained material. However, the nanocrystalline materials exhibited more uniform corrosion morphology in an acidic medium (the coarse-grained material suffered excessive intergranular corrosion) and superior localized corrosion resistance, attributed to the fine grain size and homogeneity of the nanocrystalline material.

Since majority of the synthesis methods produced nanocrystalline materials in a powder form, the total surface area available can be accurately controlled by controlling the particle size and porosity in the samples. One can consolidate the material to full density for best mechanical properties, or to a highly porous structure to obtain a large surface area, or to an intermediate value of porosity, Beck and Siegel [127] have shown that the chemical reactivity of nanocrystalline TiO$_2$ that has been only lightly consolidated is significantly higher than that in other commercially available TiO$_2$ samples. Nanocrystalline samples do not only have the increased activity, but the high activity is retained for a longer time than in commercial coarse-grained samples. This has been attributed to the large surface area of the nanocrystalline materials combine with its wurtzite structure and its oxygen-deficient composition.

There has been an increased activity in this area recently [128-130]. A new class of Pd-Fe alloy, showing continuous solid solubility at all compositions, is shown to have a high degree of H$_2$ permeation through the membrane material without experiencing poisoning by CO, H$_2$S and H$_2$O, which is commonly encountered in membrane materials that are used for H$_2$ separation. Hydrogen absorbing alloys (FeTi, LaNi$_5$, Mg$_2$Ni, and other Mg-based materials) in the nanocrystalline form show much better hydrogen absorption properties than their polycrystalline counterparts. Further
improvement is accomplished by modifying the metal powders with a small amount (<1 wt. %) of a catalyst, such as Pd, present in the form of small clusters or particles dispersed on the surface of the absorbing materials [128]. Their appears to be a lot of potential in developing improved catalytic materials for the industry. By controlling the processing parameters during the synthesis/production of nanocrystalline materials, one can fine-tune various crystalline structural parameters such as lattice parameters, defect concentration, surface chemistry, and compositional variations. Further, one can control the structure of not only the catalytic material, but also their support. The nanoporous support design could further enhance the overall catalytic processes through increased activity, better selectivity, improved stability, and greater poisoning resistance [130].

1.8. Applications of Nanomaterials

Nanocrystalline materials are novel materials, which are not only scientifically interesting but also hold great potential for varied applications. These materials offer great opportunities in developing new technologies, which can improve the basic nature of the today’s existing systems. Although no component made of nanocrystalline materials is in use in any industry now, several potential applications are suggested, based on their special attributes.

1.8.1 Next-generation Computer Chips

The microelectronics industry has been emphasizing miniaturization, whereby the circuits, such as transistors, resistors and capacitors are reduced in size. By achieving a significant reduction in their size, the microprocessors, which contain these components, can run much faster, thereby enabling computations at far greater speeds. However, there are several technological impediments to these advancements, including lack of the ultra fine precursors to manufacture these components; poor dissipation of the tremendous amount of heat generated by these microprocessors due to faster speeds; short mean time to failures (poor reliability), etc nanoparticles help the industry break these barriers down by providing the manufacturers with nanocrystalline starting materials, ultra-high purity materials with better thermal conductivity, and longer-lasting, durable interconnections (connections between various components in the microprocessors).

1.8.2 Kinetic Energy Penetrators with Enhanced Lethality

The department of defense is currently using depleted-uranium (DU) projectiles (penetrators) for its lethality against hardened targets and enemy armored
vehicles. However, DU has residual radioactivity, and hence, is toxic (carcinogenic), explosive and lethal to the personnel who use them. However, some of the important reasons for the continued use of DU penetrators are that they possess a unique self-sharpening mechanism on impact with a target and the lack of suitable non-explosive, non-hazardous replacement for DU. Nanocrystalline tungsten heavy alloys lend themselves to such a self-sharpening mechanism because of their unique deformation characteristics, such as grain-boundary sliding. Hence, nanocrystalline tungsten heavy alloys and composites are being evaluated as potential candidates to replace DU penetrators.

1.8.3 Better Insulation Materials

Nanocrystalline materials synthesized by the sol-gel technique results in foam like structure called an “aero-gel”. These aero gels are porous and extremely lightweight; yet they can withstand 100 times their weight. Aero gels are composed of three-dimensional, continuous networks of particles with air (or any other fluid, such as a gas) trapped at their interstices.

1.8.4 Low-cost flat Panel Displays

Flat-panel displays represent a huge market in the laptop (portable) computers industry. However, Japan is leading this market, primarily because of its research and development efforts on the materials for such displays. By synthesizing nanocrystalline phosphors, the resolution of these display devices can be greatly enhanced and the manufacturing costs can be significantly reduced. Also, the flat panel displays constructed out of nanomaterial possess much higher brightness and contrast than the conventional ones owing to their enhanced electrical and magnetic properties.

1.8.5 Elimination of Pollutants

Nanocrystalline materials possess extremely large grain boundaries relative to their grain size. Hence, nanomaterials are very active in terms of their chemical, physical and mechanical properties. Due to their enhanced chemical activity, nanomaterials can be used as catalysts to react with such noxious and toxic gases as carbon monoxide and nitrogen oxide in automobile catalytic converters and power generation equipment to prevent environmental pollution arising from burning gasoline and coal.
1.8.6 High Energy Density Batteries

Conventional and rechargeable batteries are used in almost all applications that require electric power. The applications include automobiles, laptop computers, and electric vehicles, next generation electronic vehicles (NGEV) to reduce environmental pollution, personal stereos, cellular phones, toys and watches. The energy density (storage capacity) of these batteries is quite low requiring frequent recharging. The life of conventional and rechargeable batteries is also low. Nanocrystalline materials synthesized by sol-gel techniques are candidates for separator plates in batteries because of their foam-like (aero gel) structure, which can hold considerably more energy than conventional ones. Furthermore, nickel-metal hydride (Ni-MH) batteries made of nanocrystalline nickel and metal hydrides are envisioned to require far less frequent recharging and to last much longer because of their large grain boundary (surface) area and enhanced physical, chemical and mechanical properties.

1.8.7 High-Power Magnets

The strength of a magnet is measured in terms of coercivity and saturation magnetization values. These values decrease with the grain size and increase with the specific surface area (surface area per unit volume of the grains) of the grains.

1.8.8 High-Sensitivity Sensors

Sensors employ their sensitivity to the changes in various parameters they are designed to measure. The measured parameters include electrical resistivity, chemical activity, magnetic permeability, thermal conductivity and capacitance. All of these parameters depend greatly on the microstructure (grain size) of the materials employed in the sensors out of nanocrystalline materials are made smoke detectors, ice detectors on aircraft wings, automobile engine performance sensor.

1.8.9 Automobiles with Greater Fuel Efficiency

Since nanomaterials are stronger, harder and much more wear-resistant and erosion-resistant, they are presently being envisioned to be used as spark plugs. These electrodes render the spark plugs longer-lasting and combust fuel far more efficiently and completely. A radically new spark plug design called the rail plug is also in the prototype stages.

1.8.10 Longer-Lasting Satellites

Satellites are being used for both defense and civilian applications. These satellites utilize thruster rockets to remain in or change their orbits due to a variety of
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factors including the influence of gravitational forces exerted by the earth. Hence, these satellites are repositioned using these thrusters. The life of these satellites, to a large extent, is determined by the amount of fuel they can carry on board. In fact, more than \( \frac{1}{3} \) of the fuel carried aboard by the satellites is wasted by these repositioning thrusters due to incomplete and inefficient combustion of the fuel, such as hydrazine.

1.8.1 Longer-Lasting Medical Implants

Currently, medical implants, such as orthopedic implants and heart valves are made of titanium and stainless steel alloys. These alloys are primarily used in humans because they are bio-compatible, i.e., they do not adversely react with human tissue. In the case of orthopedic implants (artificial bones for hip), these materials are relatively non-porous. For an implant to effectively mimic a natural human bone, the surrounding tissue must penetrate the implants, thereby affording the implant with the required strength. Since these materials are relatively impervious, human tissue does not penetrate the implants, thereby reducing their effectiveness.

1.8.12 Ductile and Machinable Ceramics

The characteristics of ceramics have discouraged the potential users from exploiting their beneficial properties, however, with a reduction in grain size; these ceramics have increasingly been used. Zirconia, a hard, brittle ceramic, has even been rendered super plastic, i.e., it can deformed to great lengths (up to 300\% of its original length). However, these ceramics must possess nanocrystalline grains to be super plastic.

Nanocrystalline materials are novel materials, which are not only scientifically interesting but also hold great potential for various applications. Their properties are different from and often superior to those of conventional coarse-grained polycrystalline materials and also amorphous alloys of the same composition. It has been shown that by decreasing the grain size to nanometer levels, traditionally soft and ductile metals can be made very hard and strong and conventional ceramics, which are brittle, can be made to deform plastically like metals.

1.9 Literature Review on DMS Nanoparticles

Major development in nanostructuring of semiconductors can be traced back to about 1970 when Esaki and his collaborators [1] at IBM in USA, produced quantum wells of GaAs and AlGaAs by alternately stacking these two materials on atomic scales. Molecular beam epitaxy (MBE) was used to produce such novel
structures. Here the charge carriers are periodically confined in the plane of the film or in the growth direction due to change in potential that will be faced at alternate material (GaAs or AlGaAs). Obviously, by cutting a thin film lithographically, one can obtain a wire and by cutting the wires lithographically quantum dots can be obtained.

Because of the practical difficulties, until 1980, research on semiconductor quantum devices was restricted only to a few laboratories. In 1980, Akimov and collaborators [131] at Ioffe physical technical institute in St. Petersburg observed that in glassy material containing CdS during uneven quenching a variety of colors were produced. These could be explained only by assuming that CdS particles of different sizes were present. In 1984, Brus [132] in USA developed a theory based on effective mass approximation (EMA), which qualitatively explains the size dependence of the optical properties of semiconductor nanoparticles, which could be obtained in colloidal solution or could be grown in polymer matrix. Sudden increase in the activity of nanoparticles research after about 1982 was obvious. It was realized that nanoparticles could be produced by different means other than MBE combined with lithography which was a costly affair. It is known that Nanocrystalline semiconductor (a few nm) exhibits the "quantum confinement effect" [132-135] and possesses physical properties that were intermediate between those corresponding to the bulk solid and molecules. Another important factor associated with nanocrystallites was the large surface to volume ratio, which results in electronic states with in the band gap which results in electronic states with in the band gap semiconductor [101]. Most studies on the nanocrystalline semiconductors belong to the II-VI group.

Bhargava et al [136] showed that the nanosize semiconductor crystallites have changed properties, such as an increased energy band gap which results from quantum confinement [136,137]. They have reported that the optical properties of ZnS semiconductor nanocrystals doped with Mn isoelectronic impurities [136,138]. The Ni²⁺ ion d-electron states act as efficient luminescent centers while interacting strongly with the s-p electronic states of the host nanocrystals into which external electronic excitation is normally directed. The electronic interaction provides an effective energy transfer path and leads to high luminescent efficiencies at room temperature.

Ekimov et al.[139] have studied the size effect in low dimensional semiconductor structures of CdS. They have shown both, theoretically and
experimentally, that the shallow impurity and defect state delocalize in microcrystal of small size. Apart from this the study has revealed the role of charged surface states. Nanoparticles have a large number of surface atoms compared to the bulk. Therefore a surface study of nanoparticles also has become quite important. Typically such small particles contain few atoms to few thousand atoms. Therefore depending upon the size of the particles and the constituting elements, ionization potential, elastic properties, magnetic properties, optical properties, bonding, melting point etc. change drastically. Such studies have been carried out by Kulkarni [140] on a number of II-VI semiconductors and oxides. A large number of methods have evolved for synthesizing nanoparticles.

Atay et al.[141], investigated the CdS and CdS:Ni films (at the Ni percentages of 10 and 20) were deposited on glass substrates by ultrasonic spray pyrolysis (USP) technique at a substrate temperature of 300 ± 5°C. The effect of Ni incorporation on the film properties was presented. The variations of conductivities of CdS and CdS:Ni films were investigated depending on the temperature and applied voltage in dark and light conditions. The film structures were studied by X-ray diffraction (XRD). The crystallinity was spoiled with increasing Ni concentration, and a shift to amorphous structure was seen. Surface morphologies of the films were studied by scanning electron microscopy (SEM). The most homogeneous surface was seen in CdS films. Elemental analyses of all films were also studied by energy dispersive X-ray spectroscopy (EDS).

Chandra Mohan et al.[142] studied the Ni-doped CdS thin films were prepared by 90 keV Ni$^{2+}$ implantation at room temperature. Ni-ion implantation induced modifications in structural, optical, and morphological properties were studied for a wide range of impurity concentrations (1.86 – 10.19 at. %). Addition of Ni$^{2+}$ ions does not lead to any structural phase transformation or formation of metallic clusters or secondary phase precipitates. However, it induces structural disorder leading to a reduction in the optical band gap from 2.39 to 2.28 eV following Ni implantation up to 3×10$^{16}$ ions cm$^{-2}$. This was addressed on the basis of band tailing due to the creation of localized energy states and implantation induced grain growth. Moreover, Ni-doping was found to modify the luminescence properties by creating shallow acceptor states.

Tang et al.[143] evaluated the high quality Cu (I)-doped CdS [CdS:Cu (I)] nanocrystals were synthesized by thermo analysis of metal acetylacetonate complexes
in n-dodecanethiol. The optical emission of the doped nanocrystals was observed to change from surface trap-dominant emission to Cu (I)-dominant emission with respect to the reaction time and the doping levels of Cu (I) ions in CdS particles. The maximum photoluminescence quantum yields of the CdS:Cu (I) nanocrystals could reach 15.8%. More interestingly, these doped nanocrystals could self-assemble into highly ordered superlattices depending on the doping levels of the Cu (I) ions. A possible explanation for the formation of the CdS: Cu (I) nanocrystal superlattices were dipole–dipole interactions between the adjacent nanocrystals.

Ubale et al.[144] studied in ternary semiconductor nanostructured composite materials have attracted the interest of researchers because of their photovoltaic applications. Thin films of (NiS)x(CdS)1-x with variable composition (x = 1–0) had been deposited onto glass substrates by the successive ionic layer adsorption and reaction (SILAR) method. As grown and annealed films were characterized by X-ray diffraction, scanning electron microscopy and EDAX to investigate structural and morphological properties. The (NiS)x(CdS)1-x films were polycrystalline in nature having mixed phase of rhombohedral and hexagonal crystal structure due to NiS and CdS respectively. The optical and electrical properties of (NiS)x(CdS)1-x, thin films were studied to determine composition dependent band gap, activation energy and photoconductivity. The band gap and activation energy of annealed (NiS)x(CdS)1-x film decrease with improvement in photosensitive nature.

Siva Kumar et al. [145] investigated the pure and Ni (2 at. %) doped cadmium sulfide (CdS) nanoparticles have been synthesized by chemical co-precipitation method at room temperature. Effect of Ni doping on CdS compound semiconductors has been analyzed using X-ray diffractometer, transmission electron microscope, energy dispersive spectroscopy, Raman and optical absorption studies. X-ray diffraction study confirmed the structure of the obtained nanoparticles to be single-phase zinc blende with the diffractions from (111), (220) and (311) planes. Energy dispersive spectroscopy study confirmed the presence of Ni in the CdS lattice. The average particle size obtained from the transmission electron microscopy studies were in agreement with the crystallite size calculated from X-ray diffraction data. The optical studies exhibited a clear red shift of absorption edge as a function of Ni doping.

Recently Thambidurai et al.[146] fabricated the Ni-doped CdS quantum dots have been prepared by chemical precipitation technique. The X-diffraction results
indicated that the particle size of Ni-doped CdS nanoparticles was smaller than that of undoped CdS and no secondary phase was observed. The average grain size of the nanoparticles was found to lie in the range of 2.7–4 nm. The compositional analysis results show that Cd, Ni, and S were present in the samples. HRTEM studies reveal that the average particle size of endowed and Ni-doped CdS quantum dots was 2 and 3 nm, respectively. Raman spectra shows that 1LO, 2LO, and 3LO peaks of the Ni-doped CdS samples were slightly red shifted when compared to that of undoped CdS. The absorption edge of Ni-doped CdS nanoparticles was found to shift towards the higher-wavelength (red shift) side when compared to that of undoped CdS and the band gap was observed to lie in the range of 3.79–3.95 eV.

Most studied nanocrystalline semiconductors belong to the II-VI groups, as they are relatively easy to synthesize and are generally prepared as particulates and in thin film forms. CdS is an important II-VI compound semiconductor with energy band of 2.42 eV and is used as a window material for solar cell devices [147]. It has typical response time of about 200 µs and sense in the wavelength range 1-3 µm. The effect of temperature for these two materials (PbS, CdS) shows opposite behavior. In case of PbS, the band gap decreases with decrease in temperature where as it remains constant in CdS. In view of the interesting size quantization effect exhibited by Ni doped CdS nanostructures, the author has chosen this system for the present investigation.

1.10. Objectives and Scope of the Present Work

CdS is the one of the important group II-VI compounds with wurtzite structure with an energy gap of 2.42 eV (at room temperature) and has been widely used in the fabrication of solar cells, photo detectors. The energy gap of this material falls on the visible range. During the last few decades DMS of A_{(1-x)}^{II}Ni_{x}B^{VI} type, where A^{II} = Zn, Cd, Hg and B^{VI} = S, Se,Te, alloys have been extensively studied. Numerous reports have devoted to either semiconducting magnetic properties of only the selenids and tellurides. However, studies on sulphide based DMS are very few of this, a systematic few investigation was carried out on sulphide based II-VI DMS in the present study. The interest in the Cd_{(1-x)}Ni_{x}S is based on their outstanding magneto-optical on photoluminescence properties caused by a strong s, p-d exchange interaction between electron or hole band states and Ni^{2+} 3d electron states. Magnetization and magnetic susceptibility measurements are important to understand the exchange interaction in DMS.
Chapter-I

Introduction

Though CdS:Ni has been studied by a few workers in nano crystalline form, a complete characterization over a wide range Ni concentration has not been reported. In view of the spectral phenomena exhibited by Cd\(_{1-x}\)Ni\(_x\)S nano crystals and realizing their application potential, a systematic investigation on the preparation and characterization of the technologically promising Cd\(_{1-x}\)Ni\(_x\)S system has been undertaken in the present work. Therefore, an attempt is made to carry out a comprehensive study on the preparation and characterization studies on Cd\(_{1-x}\)Ni\(_x\)S system.

In the present work, synthesis and characterization of undoped CdS and Ni doped CdS nano crystals ranging from 2% at to 10% have been studied. The main objectives are

1. Preparation of the undoped CdS and Ni doped CdS nano particles by a simple chemical co-precipitation method.
2. Study of structure of undoped CdS and Ni doped CdS nano particles by X-ray diffraction (XRD) patterns and determination of nano particles size with scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM) techniques. Also, chemical analysis has been carried out by energy dispersive analysis (EDAX).
3. Study of molecular information and optical band gap of the undoped CdS and Ni doped CdS nanoparticles by fourier transform infrared spectroscopy (FTIR) and UV absorption spectra.
5. To study magnetic properties by vibrating sample magnetometer (VSM) and electron paramagnetic resonance (EPR) measurements.
6. Thermal properties have been studied by thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements.

The results of the investigations and a detailed discussion are presented in the thesis. The thesis consists of five chapters.

The first chapter highlights the importance of diluted magnetic semiconducting nanoparticles with special emphasis on their enchanting properties and unique applications and includes the scope of the present work.
Chapter-1 Introduction

The second chapter represents the preparation methods of undoped and Ni doped CdS nanoparticles followed by a detailed description of the experimental techniques which are used in the present work.

The third chapter deals with the results of the different characterization studies on undoped CdS nanoparticles.

The results of the various characterization studies on nickel (Ni) doped CdS nanoparticles are presented along with relevant discussions in the fourth chapter.

The fifth chapter deals the summary of the results and the conclusions drawn from the present work and the scope for future work.
References


### References


Chapter 1

References


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