

## 1. INTRODUCTION

We introduce here in this chapter the actual work done by the candidate alongwith giving some background information related to the present topic of research.

### 1.1. Crystalline Solids

Solids can be classified into two broad categories as crystalline and amorphous. Crystalline solids are three dimensional analogues of a brick wall. They have a regular structure in which the particles pack in a repeating pattern from one edge of the solid to the other. Amorphous solids (literally "solids without form") have a random structure with little if any long-range order. Polycrystalline solids are an aggregate of a large number of small crystals or grains in which the structure is regular, but the crystals or grains are arranged in a random fashion. The extent to which a solid is crystalline has important consequences on its physical properties. Solids can be classified on the basis of the bonds that hold the atoms or molecules together. Accordingly the solids can be categorized as atomic, molecular, covalent, ionic or metallic. Molecular solids are characterized by relatively strong intramolecular bonds between the atoms

that form the molecules and much weaker intermolecular bonds between these molecules. Because of the relatively weak intermolecular bonds, molecular solids are often soft substances with low melting points. Covalent solids form crystals, there are no distinct molecules or clusters within the structure but can be viewed as a single giant molecule made up of an almost endless number of covalent bonds. Because of all the bonds in this structure are equally strong, covalent solids are often very hard and they are notoriously difficult to melt. Ionic solids are made up of oppositely charged ions, which are held together by the strong force of attraction between ions of opposite charge. The force of attraction  $F = \frac{q_1 q_2}{r^2}$  where  $q_1$  and  $q_2$  are the charges of oppositely charged ions separated at a distance  $r$ . Because this force of attraction depends on the square of the distance between the ions, the strength of an ionic bond depends on the radii of the ions that form the solids. As these ions become larger, the bonds become weaker. But the ionic bond is still strong enough to ensure that salts have relatively high melting points and boiling points. Finally metallic solids are made up of metal atoms which have loosely held outer electrons which are somewhat free from their positive cores and form a continuous dissociated sea of negative charge, binding the positive cores together.

Single crystal is one in which there is almost infinitely long arrangement of atoms or molecules with certain symmetry characteristics of the material. When we say infinite distance, it means a length many times larger than the distance between two atoms. A thin material created

by an atom/molecule/ion cluster of species by condensation process is defined as a thin film. Precisely if the thickness of the substance is less than the electron mean free path then the substance behaves as thin films. Ultrafine microstructures having an average phase or grain size on the order of a nanometer ( $10^{-9}\text{m}$ ) are classified as nanostructured materials.

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

Nanotechnologies are the design, characterization, production and application of structures, devices and systems by controlling shape and size on the nanoscale.

## **1.2. Nanocrystals**

Nanoparticles can come in a wide range of morphologies. They are nanorods, nanosheets, nanotubes, nanoplatelets, nanowhiskers, nanorings, nanobelts, etc. Nanophase materials are three dimensionally modulated, synthetic materials with average grain, phase, or other structural domain sizes below 100nm. Interest in them has increased rapidly during the past few years with successive demonstrations that their properties are different from and frequently superior to those of conventional materials that have phase or grain structures on much coarser size scales [1]. Also due to the high surface-to-volume ratio, these materials are expected to demonstrate unique mechanical, optical, electronic and magnetic properties [2]. Nanomaterials are not new.

However the understanding that certain preparations of oxides, metals, ceramics and other substances or nanomaterials is relatively recent. Carbon black is a nanomaterial that is used in car tyres to increase the life of the tyre and provide the black colour. This material was discovered in the early 1900s. Fumed silica, a component of silicon rubber, coatings, sealants and adhesives, are also a nanomaterial. It became commercially available in the 1940s. With the advent of the advanced microscopic analysis techniques, new nanomaterials have been developed much more systematically and with a greater understanding. Interest in nanomaterials was already evident before Feynman's speech [3] or Drexler's book [4] which defined the new age of nanotechnology. However, it was realized only at about this time that the particle size of carbon black and fumed silica is of nanometer dimensions. In typical nanomaterials, the majority of the atoms are located on the surface of the particles, whereas they are located in the bulk of conventional materials. Thus the intrinsic properties of nanomaterials are different from conventional materials, since the majority of atoms are in a different environment. Nanomaterials represent almost the ultimate in increasing surface area. As explained already about the surface to volume ratio applications, this can be exploited for a variety of structural and non-structural applications. In aerospace and automotive applications, for example, materials made from metal and oxides of silicon and germanium exhibit superplastic behaviour undergoing elongations from 100 to 1000 per cent before fatigue. This is because the individual

nanosized particles can expand relative to each other. Some nanomaterials are exceptionally strong, hard and ductile at high temperatures. However, they are chemically very active because the number of surface molecules or atoms is very large compared with the molecules or atoms in the bulk of the material. In nanophase materials a variety of size related effects can be incorporated by controlling the sizes of the constituent components [5-8]. Semiconductor nanomaterials are currently also considered to have technological applications in optoelectronic devices such as semiconductor quantum dots and photodiodes owing to the phenomenon of 'quantum size effects' caused by the spatial confinement of delocalized electrons in confined grain sizes [9-11]. Magnetic applications of nanostructured materials include fabrication of devices with giant magneto resistance effects, the property used by magnetic heads to read data on computer hard drives as well as the development of magnetic refrigerators that use solid magnets as refrigerants rather than compressed ozone destroying chlorofluorocarbons[12,13]. In addition nanostructured metals and ceramics seem to be candidates for new catalytic applications[14,15]. Bandgap engineering by size and dimension quantization is important because it leads to electrical, optical, magnetic, optoelectronic and magneto optical properties substantially different from those observed from the bulk materials[16]. As an example quantum dots can be developed to emit and absorb a desired wavelength of light by changing

the particle diameters. This feature allows the construction of a finely tunable and efficient semiconductor laser.

### 1.3. ZnO and CdO

Most of the group II-VI binary compound semiconductors crystallize in either cubic zinc-blende or hexagonal wurtzite structure where each anion is surrounded by four cations at the corners of a tetrahedron and vice versa. ZnO is a II-VI compound semiconductor. The crystal structures shared by ZnO are wurtzite, zinc blende and rock salt. At ambient conditions, the thermodynamically stable phase is wurtzite. The zinc blende ZnO structure can be stabilized only by growth on cubic substrates and the rock salt. ZnO is not really a newly discovered material. Research on ZnO has continued many decades with interest following a roller coaster pattern. The semiconductor ZnO has gained substantial interest in the research community in part because of its large exciton binding energy(60meV) which could lead to lasing action based on exciton recombination above room temperature semiconductor field with studies of its lattice parameter dating back to 1935 by Bunn[17], detailed optical studies in 1954 by Mollwo[18] and its growth by chemical vapor transport in 1970 by Galli and Coker[19].

The growth of bulk ZnO crystals is mainly carried out by three methods: hydrothermal[20-22], vapour phase [23-26] and melt growth [27]. Because of its high vapour pressure, growth of ZnO from the melt

is difficult and growth by vapour phase deposition is difficult to control. The low supersaturation of the solution during hydrothermal reaction favors crystal growth. However, the hydrothermal crystals inevitably incorporate alkali metals (K and Li) and small amounts of metallic impurities from the solution. The hydrothermal method uses ZnO single crystal seeds (suspended by Pt wire) and sintered ZnO strings together with a KOH and LiOH aqueous solutions are used as a nutrient. Properly polished hydrothermal ZnO exhibits optical properties similar to the vapor phase grown material. A method which produces very high quality bulk ZnO wafers is based on vapor transport. In this method the reaction takes place in a nearly closed horizontal tube. Pure ZnO powder is used as the ZnO source. As mentioned the third method for producing bulk ZnO is that of melt growth which is employed at Cermet, Inc. The Cermet, Inc. melt method is based on a pressurized induction melting apparatus. Zinc oxide powder is used as the starting material.

Sapphire substrates are commonly used for ZnO heteroepitaxial growth. In addition, ZnO and related oxides have been grown on Si[28], SiC[29], GaAs[30,31], CaF<sub>2</sub>[32] and ScAlMgO<sub>4</sub> [33]. Single crystal ZnO films have been grown on sapphire with a high degree of surface flatness, which is essential for device fabrication. The ZnO layers have been grown on sapphire by using a variety of growth techniques, including PLD, MOCVD[34] and MBE[35,36].

One of the most popular growth techniques for early ZnO investigations was sputtering(dc sputtering, rf magnetron sputtering and reactive sputtering). As compared to sol gel and chemical vapor deposition[37-39], the magnetron sputtering was a preferred method because of its low cost, simplicity and low operating temperature[40]. ZnO films grow at a certain substrate temperature by sputtering from a high purity ZnO target using a rf magnetron sputter system. For piezoelectric studies ZnO films have been deposited on diamond[41], glass, GaAs and Si substrates [44-47]. Kim et al [48] reported high quality single crystal ZnO films prepared on sapphire by rf magnetron sputtering. In the sputtering growth of oxide films,  $O^{2-}$  ions are mainly responsible for the resputtering phenomenon[49,50]. The stress in the sputtered ZnO was investigated as a function of the substrate temperature in the range of 250-450°C, the sputtering pressure and the type of substrates(Silicon, GaAs) [51-53]. Post deposition annealing also has been used to relieve the stress and improve the structure and optical properties of the sputtered ZnO films[54,55].

The main advantage of molecular beam epitaxy is its precise control over the deposition parameters and in situ diagnostic capabilities. For ZnO thin film deposition by MBE, Zn metal and  $O_2$  are usually used as the source materials. High purity Zn metal is evaporated from an effusion cell, where the cell temperature can be varied to examine the effect of the Zn flux on the growth rate and material properties. Successful growth of ZnO films by using hydrogen peroxide vapor as a

source of active oxygen has also been reported[56]. RF radical sources are employed by most groups nowadays because of the high reactivity of oxygen radicals produced and reasonable oxygen pressures. The effect of substrate offset angle on MBE growth of ZnO on c-plane sapphire were investigated by Sakurai et al.[57]. Nitridation of sapphire substrate was also used to improve the quality of ZnO films grown by plasma assisted MBE[58]. The control over the ZnO surface polarity has also been achieved on GaN substrates by plasma assisted MBE[59]. GaN is a closely lattice matched material to ZnO with a lattice mismatch of 1.8%. In this vein, Ko et al[60] studied the growth and characteristics of as grown and annealed ZnO thin films with buffer layers on GaN templates given by MOCVD on sapphire.

In the pulsed laser deposition method, high power laser pulses, are used to evaporate a material from a target surface such that the stoichiometry of the material is preserved in the interaction. Single crystal ZnO has been used to grow high quality ZnO thin film very recently. A pure Zn metal is used only in rare cases[61,62]. The properties of the ZnO films depend mainly on the substrate temperature ambient oxygen pressure and laser intensity. Sankur and Cheung[63] and Nakayama[64] have reported on high quality ZnO growth by PLD. However the influence of the growth conditions on the ZnO properties was studied much later[65-68].

Among other growth methods, CVD technology is particularly interesting not only because it gives rise to high quality films but also

because it is applicable to larger scale production. When metal organic precursors are used, the technique is MOCVD, metal organic vapor phase epitaxy or organometallic vapor phase epitaxy (OMVPE). In the case of hydride or halide precursors, the technique is named hydride or halide CVD or VPE[69,70]. In the CVD method ZnO deposition occurs as a result of chemical reactions of vapor phase precursors on the substrate, which are delivered into the growth zone by the carrier gas. The reaction takes place in a reactor where a necessary temperature profile is created in the gas flow direction. For hydride VPE growth of ZnO, hydrogen was employed as a carrier gas[71-73]. The ZnO films grown by this method show quite high crystal, electrical and luminescence properties [74,75]. For ZnO growth, MOCVD/MOVPE technique typically involves the use of metal alkyls, usually dimethyl zinc(DMZn) or diethyl zinc(DEZn) in combination with a separate source of O<sub>2</sub> and argon or nitrogen as a carrier gas. In earlier investigations O<sub>2</sub> or H<sub>2</sub>O were used as oxygen precursors [76,77]. However, DEZn and DMZn, are highly reactive with O<sub>2</sub> and water vapor so that severe premature reaction in the gas phase occurs in the cold zone of the reactor, resulting in the formation of white powder, that degrades the film quality. Nevertheless, great progress has been made in ZnO growth by MOCVD recently. For group VI precursor a variety of oxygen compounds were employed; isopropanol (i-PrOH)[78,79], tertiary butanol(t-BuOH)[80-83], acetone[84], Na<sub>2</sub>O, etc[85-87]. Kirchner et al[88] have reported direct comparison of MOVPE growth of ZnO layers on c-plane sapphire using

i-PrOH and t-BuOH as oxygen precursors and DEZn as a Zinc source. Great potential of nitrous oxide for MOVPE of ZnO was demonstrated by Ogata et al[89]. Low reactivity allows one to grow ZnO films at a high substrate temperature that results in high crystal perfection and good optical quality of the material. High quality homoepitaxial ZnO layers were grown on bulk ZnO substrates by using Na<sub>2</sub>O and DEZn [90]. The improvement of MOCVD technology also gave rise to great progress in the quality of ZnO layers grown with the use of DEZn and O<sub>2</sub>. With the use of different precursor systems, the MOCVD/MOVPE method was successfully applied to the catalyst free growth of ZnO nanowires on various substrates such as Si, GaN/sapphire [91,92], c-plane sapphire [93,94] and GaAs [95].

Controlled growth of different dimensional nanostructures such as 1D nanowires, nanotubes or 2D nanosheets and nanodiscs and 3D nanocrystals or nanoparticles are of great importance in studying the physical properties of nanomaterials or constructing nanodevices[96]. Bing Guo et al[97] studied the time resolved PL study of ZnO thin film grown on a Si substrate. Using zinc chloride as source material, Xu et al[98] fabricated ZnO nanowires and nanorods by vapor phase transport. ZnO based varistor materials have been synthesized using colloidal suspension and centrifugal separation method[99,100]. Rao et al prepared oxide nanomaterials using microwave assisted solvothermal method[101]. Electrical properties of thin films and optical properties of

nanostructures were studied by Grundmann et al.[102]. MBE technique was used by Iwata et al [103] to grow ZnO layers and to study the bandgap energy. ZnO thin films were deposited on Si substrate by radio frequency (rf) magnetron sputtering from metallic zinc target by Ondo et al[104]. Undoped and Bi-doped nanocrystalline ZnO was prepared by the inert gas condensation method by Ce-Wen Nan et al.[105]. The electrical properties were discussed using impedance spectroscopy. Lee et al[106] prepared ZnO thin films by DC or rf magnetron sputtering on glass substrates to study the structural, electrical and optical properties. Thin films of ZnO were deposited onto soda lime glass substrates by Martin et al [107] using the spray pyrolysis method. Lavrov[108] analysed the IR absorption spectroscopy of hydrogen related defects in ZnO crystals.

Al doped ZnO nanomaterials were grown by various techniques[109-118]. Co, Cr, Mn, Ni doped [119,120] ZnO nanomaterials were prepared and characterized. Ni doped ZnO powders were synthesized by Guangqing et al. and Zhingang Yin et al.[121,122] Various groups [123-140] worked for the magnetic behaviour of Mn doped ZnO nanocrystals and thin films. Using MBE method Mn doped ZnO were grown by Jung et al and Kwang et al[141,142]. Naoyuki Ueda et al prepared CdO[143,144] thin films on silica glass substrates by rf sputtering.

In order to realize the bandgap engineering to create the barrier layers and quantum wells in optoelectronic devices, the modulation of

the bandgap is an important requirement. The bandgap can be increased by incorporating Mg[145-147] and decreased by Cd[148,149]. One of the reports on the synthesis of  $Mg_xZn_{1-x}O$  with a Mg content of upto 33% was by Ohtomo et al [150] by PLD. It was found that MgO segregates in the wurtzite MgZnO lattice above 33% of Mg content, limiting the maximum bandgap to 3.9eV. XRD studies show that the a-axis length gradually increases and the c-axis length gradually decreases with increasing Mg content, and therefore the cell volume is hardly changed. Increasing the Mg composition further resulted in  $Mg_xZn_{1-x}O$  films in metastable cubic phase with bandgaps above 5.0eV. The Mg content strongly depends on the growth temperature and consequently showing strong dependence of bandgap energy on the growth temperature ranging from room temperature to 750°C. For narrower band gaps, which are desirable for wavelength tunability and attaining bandgaps corresponding to the visible spectrum, the  $Cd_xZn_{1-x}O$  alloy would be a good candidate because of the small direct bandgap of CdO(2.3eV). A decrease in the band gap down to 2.99eV could be achieved by incorporating  $Cd^{2+}$  with  $y=0.07$ . Ma et al [151] succeeded in depositing good quality  $Cd_xZn_{1-x}O$  thin films on glass and sapphire substrates using the DC reactive magnetron sputtering method. The samples exhibited good transmittance (over 85%) in the visible spectral range and a red-shift was observed in the PL with increasing Cd composition. The films with x less than or equal to 0.53 have single phase structures of pure  $Cd_xZn_{1-x}O$  with the c-axis perpendicular to the substrate surface, while the film with  $x=0.77$

were mixtures of a hexagonal ZnO phase and a cubic CdO phase. The bandgap of the  $Zn_{1-x}Cd_xO$  alloy films ( $0 < x < 0.53$ ) could be nonlinearly tuned from 3.28- 2.65eV with the Cd contents from  $x=0.0$  to  $x=0.53$ .  $Zn_xCd_{1-x}O$  nanostructured thin films were synthesized using spray pyrolysis method by Vigil et al.[152]. Using the same method Tabet et al[153] studied the structural and electrical characterizations of the  $Zn_xCd_{1-x}O$  thin films. Nanocantilever arrays of Cd doped ZnO were fabricated in large scale by Shao-Min Zhou et al[154]. PLD method[155-157] was used to prepare alloyed ZnCdO films. Wurtzite heterostructures were successfully grown by remote plasma enhanced metalorganic chemical vapor deposition (RPE-MOCVD) by Atsushi Nakamura et al[158]. Blue luminescence from textured ZnCdO films grown by Molecular Beam Epitaxy was observed by Keiichiro Sakurai et al[159]. MBE method was adopted by some other workers[160-164]. Using MOVPE method [165,166] ZnCdO thin films were grown. ZnCdO was also grown using PVD[167], DC reactive magnetron sputtering[168,169], spray pyrolysis[170] and MOCVD[171].

#### **1.4. Present Work**

Nanocrystals research has witnessed an exponential growth during the last two decades[172-178]. Much interest has been focused on quantum dots, which are semiconductor nanocrystals that can be ‘tuned’ to emit or absorb particular colours of light for use in solar energy or fluorescent

biological labels. Therefore, several methods have been developed for the preparation of nanocrystals[172,178, 179-183]. Recently, a solvothermal microwave method has been described for the preparation of nanometric metal and II-VI compound particles[184,185]. This method has been found to be fast and high yielding.

In nanoparticle systems with a characteristic size comparable to the excitonic Bohr radius, one expects high effective quantum efficiencies for photoluminescence due to quantum confinement. This, however, is usually not realized in the case of bare semiconductor nanoparticles due to the presence of the substantial number of surface electronic states which provide efficient nonradiative decay channels and lead to a degradation of the opto-electronic properties[173]. In this context, several investigators got interested in considering doped and co-doped semiconductor nanocrystals, two-component nanocomposites, semiconductor-dielectric nanocomposites, semiconductor-polymer nanocomposites, etc [175]. Currently, there is a widespread interest in the optoelectronic properties of nanometer sized semiconductor particles or quantum dots, which can be used as light emitters, photo-cells, nonlinear optical devices and fast optical switches[186]. It is important for such systems to have useful photoluminescence(PL) characteristics like high quantum yield, higher coherence and faster relaxation time which can then be tailored through size control. Apart from the optical properties mentioned above, nonlinear optical properties such as intensity dependent absorption are also very important to optoelectronics.

Kulkarni[187] has reviewed the results reported on the doped II-VI compound semiconductor nanoparticles. It has been demonstrated that the PL yield can be greatly enhanced by forming a two-component nanocomposite[188]. The nanocomposite(CdS-ZnO) films have very high PL yield and enhanced coherence compared to individual nanoparticles of CdS and ZnO. A similar approach with ZnO-CdO is expected to bring fruitful results.

ZnO and CdO are known to be important transparent conductive oxides(TCOs). Their nanostructures have been widely investigated because of the potential applications in serving as electrodes for nanoscale optoelectronic devices[189]. Cd doped ZnO nanowires[190] and nanocantilever arrays[191] have been prepared and studied recently. Very recently, Wang et al [192] have prepared the quasi-aligned  $Zn_xCd_{1-x}O$  single crystal nanorods by using thermal evaporation of Zn and  $CdCl_2$  on a Si substrate with the presence of Au catalyst. They observed that, with the Cd content increasing, the ultraviolet near band-edge emission was red-shifted to 407 nm from 386 nm. In the present work, we have attempted to prepare, for the first time,  $Zn_xCd_{1-x}O$  and  $Zn_xCd_{1-x}O:Mn$  nanoparticles(quantum dots) by using some simple solvothermal methods and characterize the prepared samples. The results obtained are reported in this thesis.

The topic of research has already been introduced in this chapter(Chapter1). Chapter 2 contains the details of materials used and various experimental and other methods followed in the present study.

Results obtained in the present study are provided and discussed in Chapter 3. The present research work is summarized together with providing the conclusions derived in Chapter 4. Chapter 5 presents the scope for the future. The literature cited are listed in the REFERENCES section. Finally, a brief resume of the candidate and the list of publications made by the candidate are provided in APPENDIXES section.