CHAPTER – 1
INTRODUCTION AND REVIEW OF LITERATURE

1.1. Introduction

The semiconductors play a very important role in designing present information age. A life without semiconductor is unimaginable today. The properties like negative temperature coefficient of resistance, rectification and light-sensitivity of materials in the early 19th century opened the new pathway for materials scientists. In 1833, Michael Faraday initiated the research towards semiconductor by reporting negative temperature coefficient of resistance of silver sulfide. Followed by many experimental observations and theoretical developments, John Bardeen, Walter Brattain and William Shockley successfully developed the first transistor in the Bell laboratory using Germanium semiconductor in 1947. When basic researchers started their work on integrated circuits at the end of the nineteen fifties they did not know that their work would change the lives of future generations.

The devices today continue to diminish in size in order to achieve higher speeds. Several alternative concepts are being investigated that would reduce the device size, power consumption and make use of multifunction properties of material. Moore noticed in Intel processor that the number of transistor in a chip was doubled in every 18 months, i.e. the number of electron used to handle one bit of information was reduced to half in every 18 months. This will continue only till one bit per one electron. To avoid such a problem, the researchers try to increase the degree of freedom of the electrons.

Integrated circuit and high frequency devices have been constructed on the base of semiconducting material where it has great advantage on the charge of the
electron. On the other hand the devices of mass storage of information are carried out by magnetic recording (hard disks, magnetic tapes, optical disk, etc.) using spin of electron in a ferromagnetic metal. The combination of these two degrees of freedom can result enhanced performance of the existing devices. We may then be able to use the capability of mass storage and processing of information at the same time. This branch of the electronics that tries to combine these two degrees of freedom in a single device is known as “spintronics” and the materials with this property are called as diluted magnetic semiconductors (DMS).

1.2. Diluted Magnetic Semiconductors (DMS)

Diluted magnetic semiconductor (DMS) is expected to play an important role in interdisciplinary materials science and future spintronics because of the existence of both charges and spin degree of freedom in a single material and their interplay is expected to explore novel physics and new devices. DMS are the semiconductors with feeble magnetic property. Some ions of the semiconductors are replaced by magnetic impurities.

Fig. 1.1: Ionic arrangement in semiconductor and diluted magnetic semiconductor (DMS)
The development of material with Curie temperature ($T_C$) above the room temperature is the key challenge in the establishment of spintronics as a practical technology. Dietl et al. theoretically predicted that the transition metal (TM) doped ZnO have ferromagnetic nature in room temperature [1]. The ferromagnetism with Curie temperature above the room temperature was experimentally investigated in TM ion doped ZnO material [2-5]. In addition, large electronegativity of oxygen is expected to produce strong p-d exchange coupling between band carriers and localized spins.

1.3. Zinc Oxide (ZnO)

ZnO is one of the II-VI group semiconductors with wide and direct band gap (3.37 eV) equivalent that of GaN and relatively higher and stable exciton binding energy of 60 meV at 300 K, which is almost three times larger than its competitor GaN (25 meV) [6,7]. Direct band gap materials have intrinsically high luminescence yield compared to indirect band gap materials. Due to the unusual electrical, optical, mechanical and magnetic properties of ZnO, it acts as a potential candidate material for solar energy conversion, storage devices, luminescence, electrostatic dissipative coatings, transparent UV protection films, chemical sensors, spintronic devices [8,9], antibacterial agent, photonic material [10], gas sensing [11], photo catalysts [12], etc.

Other favorable aspects of ZnO are non-toxic, cheap, relatively abundant source materials and chemically stable material. ZnO nanostructures are promising candidate in miniaturized optoelectronics and sensing devices. By alloying with CdO and MgO, the band-gap can be tuned further into UV or down into the green spectral ranges i.e. from 2.8 to 4 eV. As the morphology of nano-materials is one of the key factors that affect their properties. ZnO with different nanostructures, such as nano-tetrapods,
nano-multipods, shuttle-like, combs-like, nano-sheets, nano-tubes, nano-flowers, nano-wires, nano-rods, nano-belts or nano-ribbons, nano-needles and nanorings have been possible to synthesize. These advantages make zinc oxide to be an attractive semiconductor material for future applications.

1.4. History and Background of ZnO

Zinc was used to make brass by the Romans in the first century A.D before it was recognized as a unique element. Zn was only recognized as an element by Paracelsus in 1520 and O₂ was formally discovered in 1774 by Priestley. The Chinese however used ZnO commercially for several centuries before that. The modern history of ZnO started around the middle of the 18th century. Cramer, a German scientist discovered that it could be made by burning metallic Zn in air. The manufacture of ZnO started in France about 1840.

In 1871, ZnO was used in the paint trade due to its whiteness, fine texture and opacity. ZnO in sufficient quantities helped to hasten the development of rubber and ceramic goods as well as the paint industry. Soon after the first radio stations started broadcasting in 1920’s, ZnO crystals came into popular for their semiconductor properties [13]. A Schottky barrier was created by contacting a ZnO crystal with a copper wire, providing the rectification needed to convert the AC radio waves to DC signals.

The light emission from ZnO was gaining interest after some initial work in Germany in 1930’s [14]. Electron diffraction data on ZnO first appeared in 1935 [15]. Three years later, the first ever scanning electron microscope image was taken of ZnO crystal [16]. Temperature dependent Hall measurements of ZnO were first reported in 1954 confirming the inherently n-type nature of this material [17].
The first period of notable growth in ZnO research occurred in the mid 1960’s. The nature of the excitonic molecule in semiconductors was extensively discussed using excitonic emission in ZnO [18, 19] and ZnO phonon energies was identified in 1966 from Raman Effect studies [20].

The higher-profile works in 1970’s concentrated mainly on manufacture and characterization of ZnO devices. Theoretical and experimental work also continued to offer further insight into the optical and electrical character of the material through a variety of techniques such as cathode-luminescence (CL) [21], capacitance-voltage studies (CV) [22], electrical conduction [23] and further work on Raman scattering [24].

The 1980’s led to a departure from characterization studies of the simpler ZnO-based devices. Many growth procedures were examined in the quest for high-quality thin films. Metal-organic chemical vapour deposition (MOCVD) [25], spray pyrolysis [26] and radio-frequency (RF) magnetron sputtering [27] were discussed for growing good quality ZnO. The group-III [28] or group-V [29] elements were doped with ZnO. The quantum-size particle growth had been also achieved [30]. In addition, an attempt on the p-type issue with doping of thin films [31] fuelled interest in ZnO. Much of the research in 1980’s attempted to resolve issues concerning a lack of satisfactory material for device fabrication. The 1980’s showed the beginning of the extensive ZnO nanostructure growth.

The advent of modern analysis tools such as atomic force microscopy (AFM) and laser interferometric analysis enabled more in-depth analysis of ZnO. Combined with the possibility to grow epitaxial layers, quantum wells and nano-rods led to a renewed interest in 1990’s. The majority of works from 1990 onward focused on high-quality growth [32], doping studies directed toward p-type ZnO [33], electrical
In the 1990’s, newer growth methods were used including pulsed laser deposition (PLD) and molecular-beam epitaxy (MBE). Look et al. worked toward fabricating high-purity bulk ZnO wafers and had success in 1998 with the vapour-phase-transport growth method. The commercially available single crystal ZnO was first produced by Eagle Pitcher Company. Bulk ZnO had been manufactured and studied since 1950s but large scale commercial material only came into the forefront in late 1990s.

Work in the early part of 2000s focused mainly on growth mechanisms and parameters. The nature of native defects incorporated from growth was studied; potential p-type dopants and the difficulties encountered in their incorporation examined extensively, together with the fundamental optical and electrical properties, and the initial breakthrough of ZnO-based light emitters achieved. Dietl et al. predicted theoretically that room-temperature ferromagnetism should exist in heavily p-type doped ZnO using modified Zener model for magnetism which initiated the research towards dilute magnetic semiconductors (DMS). The number of research areas in ZnO had mushroomed, but the goals being pursued the production of high quality, reproducible, p-type conducting ZnO for device application was perennial.

1.5. Effect of Doping and Co-doping with ZnO

Transition metals are the elements in the d-block category that belongs to the groups V-XII in the periodic table. These are metals having incomplete ‘d’ sub-shell and can easily form cations. In actual practice, the f-block lanthanide and actinide
series are also considered as transition metals and are called “inner transition metals (ITM)”. TM doping is an effective way to adjust the energy level surface states of ZnO. It can further improve its physical optical and structural properties.

Meanwhile, the solubility of Cu in ZnO lattice is limited at 4% and the Cu doping beyond the solubility limit creates the metallic clusters or secondary phase like CuO. The formation of metallic clusters or secondary phase leads to decrease in charge density of the materials. The higher doping percentage without metallic cluster is ensured by the doping of two or more favour TM elements. Ni, Co, Cr, Fe and Mn were chosen as co-dopant in addition to Cu.

In the present thesis, the following TM doped and co-doped ZnO materials were synthesized and their optical, structural, morphological, electrical and magnetic properties are characterized:

1. Zn$_{0.96}$Cu$_{0.04}$O nanoparticles with different solvents and different annealing temperatures.
2. Zn$_{0.96-x}$Cu$_{0.04}$Ni$_x$O nanoparticles (co-precipitation method).
3. Zn$_{0.96-x}$Cu$_{0.04}$Co$_x$O nanoparticles (co-precipitation method).
4. Zn$_{0.96-x}$Cu$_{0.04}$Cr$_x$O nanoparticles (co-precipitation method).
5. Zn$_{0.96-x}$Cu$_{0.04}$Fe$_x$O nanoparticles (sol-gel method).
6. Zn$_{0.96-x}$Cu$_{0.04}$Mn$_x$O nanoparticles (sol-gel method).

1.6. Review of Literature

1.6.1. Cu-doped ZnO

The properties of ZnO should be tuned for some specific needs and applications. TM doping can change its physical properties like structural, optical, electrical and magnetic properties by altering its electronic structure. The properties of
TM doped ZnO material mainly depend the kind of dopant and its concentration. Among different TM, Cu is important due to its similar electronic shell structure, physical and chemical properties to those of Zn [53]. As stated in history and background (section - 1.4), the main problem encountered by researcher was p-type conductivity in naturally n-type ZnO semiconductors. The research peoples focused their interest towards this issue on ZnO from 1980’s.

Kanai reported that Cu behaving as an acceptor in ZnO crystals and hence it could be a good candidate for creating p-type ZnO [54]. Recently, Zheng et al. prepared Cu doped ZnO powders by sol-gel method and they interpreted their results with theoretical investigation (first principle calculation). They theoretically showed that the Fermi level of ZnO shifted upwards into the valence band and exhibit p-type metallic characteristics after Cu doping. Meanwhile, the spin polarized carriers, p-d hybridization between Cu and its neighbouring O atoms, polarization of the unpaired electrons with spins near defects were responsible for noticed FM. Thus both the p-type conductivity and ferromagnetic ordering were induced by Cu doping [55]. More recently, Ghajari et al. had done similar experimental and theoretical investigation on Cu doped ZnO nanopowders and got similar results. Additionally, they found that the optical band energy was decreased when Cu doping concentration increased [56].

Kim et al. [57] studied the effect of electrical conduction on magnetic behaviour of Cu doped ZnO thin films. They found that the magnetic behaviour of the thin film was turned from paramagnetic to ferromagnetic when electrical conduction changed from n-type to p-type. The Cu doping shifted the conduction from n-type to p-type and hence the FM was induced.
Singhal et al. prepared Cu doped ZnO nanopowders by using co-precipitation method and the powder was characterized by structural and electrical properties [58]. They found that the DC electrical resistivity of the material was decreased when Cu was doped with ZnO. In addition, the average crystallite size was decreased by Cu doping. They explained the crystallite size decrease with the help of Zener-Pinning effect that the inhibited motions of grain boundaries prevent the particle growth.

A higher photocurrent for ZnO:Cu films under UV illumination was observed by Li et al. [59] and they noticed the high sensitivity and fast response and recovery times in ZnO:Cu films. Under periodic UV illumination at 380 nm the ZnO:Cu films showed stable photo-current growth and decay, so the films were potential candidate materials for UV photo detectors. They also stated that the blue–green emission of ZnO:Cu films was due to the incorporation of Cu ion. Liu et al. found that the Cu-doping ZnO/ZnS nano-rods served as a photo anode and the Cu doping enhanced photocurrent and conversion efficiency [60]. They predicted that the promoting effect of the Cu-doping on the photo anode could be attributed to the formation of intermediate energy level that allows Cu/ZnO to be activated easily in the visible area.

Reddy et al. [61] synthesized Cu doped ZnO nanopowders with the particle size in the range of ~40nm. Strong p-d mixing of O and Cu was narrowing the band and the red shift was noticed in the absorbance peak. Moreover, the Cu substitution in ZnO lattice supressed the green emission and enhanced the UV emission. Hence, they concluded that the Cu doping reduces the defects in the ZnO lattice. Wang and Lin [62] synthesized Cu doped ZnO nanoparticle sheets and it showed tunable photoluminescence. They found that the increase of Cu concentration in the ZnO lattice produced the red shift in both absorbance and photoluminescence peak. Similar enhancement in
luminescence properties was found by Sharma et al. in ZnO material by Cu doping [63]. The intensity was rapidly increased at initial Cu doping concentration and saturated at higher level (≥ 8%). They also found that the crystallinity was decreased due to the distortion created in ZnO lattice by Cu impurity.

The enhanced ammonia gas sensing property at room temperature in spray deposited thin film was reported by Mani et al. They also found that the average grain size was decreased with the increase of Cu concentration. The band gap of the film was narrowed and the transmission got decrease when Cu doping concentration increased [64]. Hu et al. studied that Cu doping in ZnO nano rod structure enhanced the formaldehyde-sensing property [65].

Gomathi sankar et al. [66] investigated the enhanced photocatalytic hydrogen production from aqueous methanol solution using ZnO with the aid of simultaneous metal deposition. They found that the addition of Cu ion effectively improved the photocatalytic hydrogen production among other metal. The photocatalytic hydrogen production using ZnO photo-catalyst with aid of simultaneous deposition of Cu was approximately 130 times better than those obtained with bare ZnO.

Thus Cu incorporation into ZnO lattice made it to be a multifunctional material by improving or modifying its properties. In addition, annealing temperature also influenced on the properties of Cu doped ZnO nanostructure. Li et al. studied the effect of annealing temperature on properties of Cu implanted ZnO nano-rod arrays. The sample was annealed for 500, 600 and 700°C and its effect on structural, optical and magnetic properties was studied. The increase of annealing temperature increased the intensity of defect related visible emission and the UV emission was suppressed. The 500°C annealed sample had maximum saturation magnetization value than other samples. The increase of annealing temperature decreased the saturation magnetization [67].
Liu et al. noticed the Cu related secondary phases at 5% of Cu doped ZnO nanoparticles and they suggested that the Cu solubility limit in ZnO lattice was around 5%. The room temperature ferromagnetism was noticed in all Cu concentration but beyond 2% of Cu doping, the saturation magnetization was decreased. The decrease of magnetization at higher doping concentration was due to the antiferromagnetic coupling between Cu pairs occurred at shorter separation distance [68]. Wei et al. reported that the TM doping beyond solubility limit let to segregation of secondary phases and the secondary phase decreased the carrier density of the material [69].

The secondary phase segregation problem is avoided by doping two or more favour TM ions simultaneously [70-72]. Therefore, the subsequent sections describe the literatures of TM ions co-doped ZnO nanoparticles.

1.6.2. Cu, Ni co-doped ZnO

The increase of saturation magnetization and the decreases of coercivity with the increase of Ni concentration were noticed by Koseolu et al. [73]. They also discussed the decrease of optical band gap by the increase of carrier concentration with increase of Ni doping concentration. Tang et al. [74] revealed the preparation of Ni and Cu co-doped ZnO nano-rods and they found that the carrier mediated room temperature ferromagnetism for all the samples. The observed room-temperature ferromagnetism could be induced by the exchange interaction between free delocalized carriers (holes from valence band) and the localized d spins of Ni and Cu ions.

Muniyandi et al. found that the Ni doping in sprayed ZnO thin films let to increase the electrical conduction as well as ethanol sensing properties at room temperature. The optical band gap of the ZnO film was decreased with the increase of Ni concentration [75]. Xu et al. also studied that the gas sensing properties of the ZnO
was enhanced by Ni doping [76]. Goswami et al. studied the structural deformation from nanoparticle to nanorods at 10 at% of Ni doping. Moreover, they also noticed that the secondary phase related to NiO was noticed after 5% of Ni doping [77]. NiO secondary phase was noticed after 4% of Ni doping and the band gap was decreased with the increase of Ni concentration [78].

Rambu et al. synthesized Ni-doped ZnO films with different nickel content on glass substrates by spin-coating and the effect of Ni concentration on the gas sensing characteristics of zinc oxide thin films was investigated. Gas sensing characteristics of Ni doped ZnO films were compared with those of pure ZnO and NiO films. Structural investigations performed by X-ray diffraction technique indicated that the studied samples are polycrystalline. Gas sensing measurements were performed and it was observed that investigated films are most sensitive to ammonia against LPG and ethanol. An increase of gas sensitivity with increase of Ni concentration was observed and it was concluded that morpho-structural changes induced by addition of Ni in ZnO structure were responsible for gas sensing characteristics. The sensitivity values of Ni doped ZnO films were higher when compare to pure ZnO and NiO [79].

1.6.3. Cu, Co co-doped ZnO

Guner et al. found that the Co implanted ZnO films exhibited ferromagnetic behavior at room temperature and have Tc value above 1000 K [80]. The magnetization increased with increasing Co concentration. The origin of observed ferromagnetism was mainly attributed to the substituted Co ions in ZnO matrix. The electrical resistivity of samples abruptly decreased from $6.44 \times 10^{-2} \ \Omega \text{cm}$ to $6.46 \times 10^{-5} \ \Omega \text{cm}$ with increasing Co concentration. The combination of structural, magnetic and electrical analysis of samples clearly showed that Co ion implantation into ZnO films...
produced the ferromagnetism above 1000 K and simultaneously increased the electrical conductivity. Sharma et al. noticed the similar enhancement in magnetization when Co was doped with ZnO. The saturation magnetization was increased with the increase of Co concentration [81].

Rajbongshi et al. studied the photo activity of ZnO and Co doped ZnO for degradation of methylene blue and phenol under UV and visible radiation flux. Co doping promoted the degradation of methylene blue and phenol under visible light irradiation and they concluded that such a high degradation was due to the decreased band gap and associated red shifted absorption of Co doped nano rods. However, its low UV radiation activity compared to ZnO could be the reduction in activity with the reduction in oxygen vacancy relative to the ZnO nanorods [82]. Kao et al. also found the similar improved photocatalytic behavior after Co doping in ZnO thin films [83].

Ganbavle et al. found that the LPG gas sensing of the ZnO thin films was enhanced by 2% of Co doping and Co doping beyond 2%, the sensing property was decreased. In addition, the 2% of Co doped ZnO thin film showed constant gas sensing response for larger time interval [84]. Arshad et al. synthesized Co-doped ZnO nanoparticles using wet chemical route. The dielectric constant and loss tangent were decreases with the increase in dopant concentration. Loss tangent showed the peaking behavior for all the samples where peak shifted towards low frequency with doping [85].

1.6.4. Cu, Cr co-doped ZnO

Pang et al. found the enhancement of room temperature ferromagnetism by Cr doping in sputtered ZnO thin films. At higher doping concentration, a secondary phase, ZnCrO$_4$ was segregated. The saturation magnetization was decreased by secondary
phase and the coercivity was slightly increased [86]. Aljawfi et al. synthesized Cr doped ZnO nano structures by sol-gel route and characterized by electrical and magnetic. The samples exhibited room temperature ferromagnetic (RTFM) behavior, which had been discussed based on BMP model and effect of grain/grain boundary structure. The saturation magnetization was increased by Cr doping. Dielectric constant had been explained in the light of Maxwell–Wagner interfacial model, which differentiates between the structure of grain-core and grain-boundary [87].

The excellent photocatalytic activity by Cr doping in ZnO nanorod arrays was studied by Chang et al. They suggested that the improved photocatalytic was due to the increase of surface oxygen vacancies and modification of band gap. The band gap was narrowed (red shift in absorption band) by Cr doping and hence the photocurrent got increase [88].

Al-Hardan et al. studied the acetone vapour sensing properties of Cr doped ZnO thin films and the effect of Cr concentration on gas sensing properties was also studied. They found that 1% Cr doped thin films had maximum response, which could have been attributed to the catalyst nature of Cr ion. The Cr doping shifted the optimum operating temperature of ZnO (400°C) to low value (300°C). They also found the maximum solubility limit of Cr in the film at 3% doping [89]. In their previous work, they also found similar Cr enhanced oxygen gas sensing property of ZnO thin films and the reduced optimum operating temperature by Cr doping [90].

1.6.5. Cu, Fe co-doped ZnO

Kumar et al. identified that the photocatalytic activity of Fe doped ZnO nanopowders were much better than undoped ZnO under both UV and visible light irradiation. They also found that the 1% of Fe doped nanopowders had high degree of
dye degradation. Similarly, the Fe doping induced the room temperature ferromagnetism in ZnO nanopowders [91]. Kaur et al. also found that the Fe doping induced the ferromagnetism at room temperature and the magnetization increased with the increase of Fe concentration. Moreover, the magnetization got decreased at 5% of Fe doping [92].

Dhiman et al. studied the narrowing of band gap by Fe doping at low Fe contents, but the band gap increased at higher Fe doping level beyond 5% due to Burstein-Moss effect. The narrowed band gap by Fe doping led to enhance the photocatalytic activity of the ZnO material [93]. The improved ethanol and acetone gas sensing property by Fe doping was studied by Yu et al. in ZnO microspheres. The 1% of Fe doped ZnO sample showed maximum response, while excessive doping reduced the gas sensing response [94]. Prajapati et al. found the similar enhancement of acetone sensing by Fe doping in ZnO thin films. They also noticed maximum sensing response at 1% Fe doping [95].

Ba-Abbad et al. studied visible light photocatalytic activity of Fe$^{3+}$ doped ZnO nanoparticles. As the Fe$^{3+}$ concentration increased from 0.25 to 1 wt.%, the crystallite decreased in comparison with the undoped ZnO. The spectral absorption shifts of the visible light region (red shift) and the band gap decreases for each Fe-ZnO sample were investigated. The photocatalytic activities of the ZnO and Fe-ZnO samples were evaluated based on the degradation of 2-chlorophenol in aqueous solution under solar radiation. The samples with a small concentration of Fe$^{3+}$ ions showed enhanced photocatalytic activity with an optimal maximum performance at 0.5 wt.%. The results indicated that toxicity removal of 2-chlorophenol at same line of degradation efficiency. Small crystallite size and low band gap were attributed to high activities of Fe-ZnO samples under various concentrations of Fe$^{3+}$ ions compared to undoped ZnO [96].
1.6.6. Cu, Mn co-doped ZnO

Ravichandran et al. studied that the room temperature ferromagnetism of the Mn doped ZnO nanopowders had been increased when Mn doping concentration increased till 6%. The emission peak corresponding to NBE transition got red shift (band gap narrowing) by Mn doping. They also found that the antibacterial activity of the material increased with the increase of Mn concentration [97]. Yuan et al. found similar enhancement in ferromagnetism at room temperature by the addition of Mn with ZnO nanoparticles. They also concluded that the RTFM enhancement was due to both Mn dopant and oxygen vacancies which were created during Mn doping [98].

Sivalingam et al. found that the electrical resistivity of the sprayed ZnO thin film was decreased when Mn was doped with ZnO. Increase of Mn concentration in the film decreased the electrical resistivity as well as band gap of the material. The Mn doping also enhanced the ethanol sensing property of the ZnO thin film [99]. Ahmed et al. prepared un-doped and Mn-doped ZnO nanorods by microwave-hydrothermal method for oxygen gas sensing at room temperature. The gas sensing results revealed that the Mn-doped ZnO nanorod sensors had significantly better sensing performance than un-doped ZnO nanorod sensors due to high aspect ratio, resulting in a larger quantity of adsorbed oxygen. Therefore, the Mn-doped ZnO nanorods would be of great potential for many practical applications including gas sensors [100].

Saleh and Djaja noticed that the Mn doping enhanced the photo degradation efficiency of ZnO nanoparticles for methyl orange dye and the degradation increased with the increase of Mn doping concentration till 12 at%. The photo catalytic activity of the Mn doped ZnO was performed under both UV and visible light irradiation [101].
Sabri et al. synthesized Mn doped ZnO nanoparticles by Mechanochemical processing and studied the effect of Mn doping on emission properties of ZnO nanoparticles. Mn doping resulted in shifting of near-band-edge (NBE) emission and the reduction in the intensities of NBE, blue and green emissions. The initial red shift at lower Mn content could be due to s–d and p–d exchange interactions as well as band tailing effect whereas the blue shift at higher Mn content could be attributed to the Burstein-Moss shift. The reduction in emission intensity could be due to non-radiative recombination processes promoted by Mn ions with increasing Mn content [102].

Thus the Ni, Co, Cr, Fe and Mn dopants enhanced the RTFM, electrical conduction, gas sensing, photocatalytic properties of ZnO semiconductors similar to those of Cu dopant and the optical band gap was narrowed by the addition of transition metal in ZnO like Cu addition. Hence, Ni, Co, Cr, Fe and Mn elements are found to be suitable co-dopant elements for Cu to enhance the properties of ZnO without secondary phase segregation.

1.7. Scope and Objective

- To synthesize Ni, Co, Cr, Fe and Mn co-doped Zn$_{0.96}$Cu$_{0.04}$O nanoparticles by varying the doping concentration from 0 to 4%.
- To check phase purity of the synthesized material and to evaluate the dopant effect on structure and lattice parameters.
- To calculate average crystallite size of all synthesized material and correlate with the different properties of the material.
- To study the modifications produced by dopant on optical absorption and emission of the TM co-doped Zn$_{0.96}$Cu$_{0.04}$O nanoparticles.
To calculate optical band gap of the synthesized material and find the dopant effect on band gap.

To identify the dopant effect on dielectric properties and ac conduction properties of the synthesized nanoparticles.

To understand the origin of room temperature ferromagnetism and find dopant effect on RTFM.

1.8. Overview of thesis

In chapter 2, the methodology used for sample preparation is briefly described. Further, the experimental techniques such as XRD, SEM, Ultraviolet and Visible (UV-Vis) spectroscopy, Photoluminescence, FTIR, LCR meter and VSM are discussed in this chapter. To optimize the preparation condition, the bare material (Zn$_{0.96}$Cu$_{0.04}$O nanoparticles) was prepared using different solvents and the prepared nanoparticles undergone various annealing temperature. The influence of solvent and annealing temperature is given in chapter 3.

The effect of Ni co-dopant on structural, optical, electrical and magnetic properties of Zn$_{0.96}$Cu$_{0.04}$O nanoparticles has been arranged in chapter 4. The chapter 5 deals the Co co-dopant induced modifications on structure, optical absorption, optical emission, dielectric properties, ac conduction and room temperature ferromagnetism of Zn$_{0.96}$Cu$_{0.04}$O nanoparticles. In chapter 6, influence of Cr co-dopant on properties of Zn$_{0.96}$Cu$_{0.04}$O nanoparticles are discussed in detail. The suppression of grain surface growth by Fe dopant and the size reformed properties of Zn$_{0.96}$Cu$_{0.04}$O nanoparticles are listed in the chapter 7. The chapter 8 covers the preparation and characterization of Mn co-doped Zn$_{0.96}$Cu$_{0.04}$O nanoparticles. The chapter 9 gives the summary and suggestions for future work.
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