CHAPTER 1

REVIEW AND PREPARATION OF DILUTED MAGNETIC SEMICONDUCTORS

1.1 REVIEW OF DILUTED MAGNETIC SEMICONDUCTORS

Diluted magnetic semiconductors (DMS) are referred as semimagnetic semiconductors, with lattice partly substituted by magnetic atoms. In semiconductor devices, the information is transferred by charge carriers and in contrast, magnetic materials are utilized on the basis of electron spin in DMS. In order to develop multi functional devices, it is essential to combine both charge and spin of the electrons. In this, the spin of electrons that carries the information can be used as an added degree of freedom in novel electronic devices (Wolf et al 2001). Thus the emerging research area known as ‘spintronics’ or spin based electronics seeks to extend the properties and applications of established devices by making use of the spin of electrons in addition to their charge (Das Sarma 2001). It is possible to merge electronics, magnetic, and photonics all together; the merging of these three properties would no doubt lead to entirely new area as shown in Figure 1.1. The prospect of these exciting ventures would be greatly enhanced if semiconductors with proper properties are available. Thus, a semiconductor with ferromagnetism at room temperature has been actively searched in recent years (Jeong et al 2004).

At present, there is a lot of interest in the science and potential technological applications of spin-transport electronics or spintronics, in
which the spin of charge carriers is exploited to provide new functionality for
electronic devices (Prinz 1998; Ohno 1998). In Figure 1.2, the three types of
semiconductors are sketched. The development of spintronics i.e., magnetic
semiconductors (Figure 1.2a), which would allow signal amplification
compatible with standard semiconductor growth techniques and would open
new possibilities (Rebecca Janisch et al 2005). Existing magnetic devices, like
read heads in computer hard drives, magnetic sensors and magnetic random
access memories which exploit the giant magnetoresistance (GMR) and
tunneling magnetoresistance (TMR) effects, are largely based on the
ferromagnetic metal or metal-insulator-metal based devices (Johnson 1994;
Parkin 1993).

There are materials like, Eu- and Mn- chalcogenides and
ferromagnetic or ferromagnetic semiconducting spinels (Figure 1.2a) that
have both magnetic and semiconducting properties but they have low Curie
temperature (Tc). Also, it is very difficult to grow and is incompatible with
common semiconductor materials such as non-magnetic Si or GaAs
(Figure 1.2c) (Mauger and Godart 1986; Treitinger et al 1976; Steigmeier and
Harbeke 1970). Diluted magnetic semiconductors are alternative with non-
magnetic semiconductors, which are doped with magnetic atoms
(Figure 1.2b). There is a considerable progress in the field of DMS, and a
number of different semiconductor hosts has been explored. They can be
realized by alloying semiconductor with magnetic elements, for instance Mn.

Initially, II-VI based semiconductors such as CdTe or ZnSe were
able to accommodate large quantities of magnetic dopants like Mn or Co.
They have been studied extensively for their interesting magneto-optical
properties (Furdyna 1988). But in the II-VI compounds, antiferromagnetic
interaction dominated among Mn spins (Furdyna 1988) and it has proved the
difficulty in creating p- or n-type carriers to mediate ferromagnetic
Figure 1.1  Schematic representations of spintronics

Figure 1.2  Three types of magnetic semiconductors a) magnetic semiconductor, b) diluted magnetic semiconductor, an alloy between magnetic element and nonmagnetic semiconductor, c) nonmagnetic semiconductor with no magnetic ions
interaction. Also, the ferromagnetic property was detected at low temperature, which is not suitable for practical applications. III-V semiconductors such as GaAs or InAs are more promising for DMS. When divalent transition metal ions are doped in a trivalent III-V host lattice, holes are also introduced to mediate the observed ferromagnetic ordering in these systems. The Curie temperature ($T_C$) of III-V semiconductors based DMS goes upto ~100 K which is higher than those of II-VI DMS, but have not reached the room temperature values that are desirable for device applications (Ohno 1998; Sanvito et al 2002).

1.1.1 Ferromagnetism in DMS Materials

Oxides based DMS have been reported to be robust room temperature ferromagnets due to several distinct reasons like, possibility of tuning the lattice constant and band parameter by varying the composition of the material, the random distribution of magnetic ions over the cation sublattice leads to important magnetic effects and large electronegativity of oxygen is expected to produce strong $p$-$d$ exchange coupling between band carriers and localized spins (Mizokawa et al 2002) etc. Among the oxide based semiconductors, Zinc oxide (ZnO) and Titanium dioxide (TiO$_2$) systems have received much attention due to the existence of ferromagnetic property at room temperature. The ferromagnetic property in oxide DMS materials has been explained by given various models.

Dietl et al (2000) proposed a model called free carrier mediated exchange model and this model was based on the original model of Zener and the Ruderman-Kittel-Kasuya-Yoshida (RKKY) interaction (Fukumura et al 2005; Liu et al 2005). This model explained the ferromagnetism by exchange interaction between carriers and localized spins ie the magnetic property was mediated by the charge carriers of the materials. The transition temperature
was theoretically calculated based on this model as shown in Figure 1.3. This model is valid only for materials having high hole concentrations and not suitable for low carrier concentration.

Figure 1.3 Curie temperatures of group IV, III-V, and II-VI semiconductors (Dietl et al 2000)

To overcome the difficulties of carrier mediated exchange model, the double exchange mechanism was proposed based on the first principles ab initio calculations of the electronic structures of transition metal (TM) -doped II-VI compounds (Sato and Katayama-Yoshida 2003; Sato et al 2001a; Sato et al 2001b; Yamamoto and Katayama-Yoshida 1999; Sato et al 2001c). In the double exchange mechanism, magnetic ions in different charge states couple with each other by virtual hopping of the extra electron from one ion to the other. If the magnetic moments are in the same direction, transition metal d-band was widened by the hybridization between the spin-up states. Therefore, in the ferromagnetic configuration the band energy can be lowered by introducing carriers in the d-band. In these cases, the 3d electron in the partially occupied 3d-orbitals of the TM is allowed to hop to the 3d-orbitals of the neighboring TM, if neighboring TM ions have parallel magnetic moments. As a result, the d-electron lowers its kinetic energy by hopping in the ferromagnetic state, or the so-called double exchange mechanism (Jagadish and Pearton 2006).
The most recent model is due to Coey et al (2005), the so-called spin-split-orbit model shown schematically in Figure 1.4. The model is consistent with the observed magnetization in n-type transition metal doped ZnO. The ferromagnetic exchange is mediated by shallow donor electrons that form bound magnetic polarons, which in turn overlap to create a spin-split impurity band. Magnetic ions in different charge states are coupled by virtual hopping of the ‘extra’ electron from one ion to the other. The 3d electrons in the partially occupied 3d-orbitals are allowed to hop to the 3d-orbitals of the neighboring TM, if neighboring TM ions have parallel magnetic moments. The ferromagnetic exchange is mediated by charge carriers in a spin-split impurity band formed by extended donor states. The impurity states hybridize with the d-orbits of the transition metal elements (Jagadish and Pearton 2006).

![Figure 1.4](image)

**Figure 1.4** Schematic structure of oxide with 3d impurities and spin-split donor impurity band (a) 3d level for low $T_C$ when the splitting of the impurity band is small. (b) and (c) show the positions of the minority or majority spin 3d bands which lead to high $T_C$ (Coey et al 2005)
1.2 BASIC PROPERTIES OF ZnO

Zinc Oxide (ZnO) is a wide band gap (direct) material and presents an interesting system because of its multidirectional applications e.g. Opto-electronic displays, electrophotography, photovoltaic conversion and electroacoustic transducers etc. Its band gap is 3.35 eV at room temperature and emits in the Ultra Violet (UV) to blue spectral range. It exists in hexagonal wurtzite structure with \( a=3.25 \, \text{Å} \) and \( c=5.12 \, \text{Å} \), in which each ion is connected with four counter ions in the tetrahedral bond of \( sp^3 \) hybridization as shown in Figure 1.5. It has a large exciton bonding energy (60 meV) relative to its III-N counterparts (25 meV). Other favorable aspects of ZnO include its broad chemistry leading to many opportunities for wet chemical etching, low power threshold for optical pumping, radiation hardness and biocompatibility. Together, these properties of ZnO make it an ideal candidate for a variety of devices ranging from sensors through to ultra-violet laser diodes and nanotechnology-based devices such as displays. Table 1.1 shows a compilation of basic physical parameters for ZnO.

![Figure 1.5](image)

**Figure 1.5** The hexagonal wurtzite structure of ZnO. O atoms are shown as large white spheres, Zn atoms as smaller black spheres.
Table 1.1 Properties of Wurtzite ZnO

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameters at 300 K</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>0.32495 nm</td>
</tr>
<tr>
<td>c</td>
<td>0.52069 nm</td>
</tr>
<tr>
<td>a/c 1.602 (Ideal hexagonal structure shows 1.633)</td>
<td>u 0.345</td>
</tr>
<tr>
<td>Density</td>
<td>5.606 g/cm³</td>
</tr>
<tr>
<td>Stable Phase at 300 K</td>
<td>Wurtzite</td>
</tr>
<tr>
<td>Melting Point</td>
<td>1975 ºC</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.6, 1-1.2</td>
</tr>
<tr>
<td>Linear expansion coefficient (ºC)</td>
<td>a₀: $6.5 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>c₀: $3.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>Static dielectric constant</td>
<td>8.656</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>2.008, 2.029</td>
</tr>
<tr>
<td>Energy gap</td>
<td>3.4 eV, direct</td>
</tr>
<tr>
<td>Intrinsic carrier concentration &lt; $10^6$ cm⁻³ (max n-type doping &gt;$10^{20}$ cm⁻³ electrons; max p-type doping &lt; $10^{17}$ cm⁻³ holes)</td>
<td></td>
</tr>
<tr>
<td>Exciton binding Energy</td>
<td>60 meV</td>
</tr>
<tr>
<td>Electron Hall mobility at 300 K</td>
<td>200 cm²/Vs</td>
</tr>
<tr>
<td>for low n-type conductivity</td>
<td></td>
</tr>
<tr>
<td>Hole effective mass*</td>
<td>0.59</td>
</tr>
<tr>
<td>Hole Hall mobility at 300 K for low p-type conductivity*</td>
<td>5-50 cm²/Vs</td>
</tr>
</tbody>
</table>

*Values still in debate (reproducibility of p-type conductivity is yet to be verified).
1.3 BASIC PROPERTIES OF TiO$_2$

TiO$_2$ exists in a number of crystalline forms and the most important of which are anatase and rutile. Unit cells of the structures are shown in Figure 1.6. The relative stability of rutile and anatase at ambient conditions is a controversial topic in the literature, both from the experimental and theoretical points of view (Muscat et al 2002; Calatayud et al 2001; Ranade et al 2002; Banfield et al 1993). But rutile is the most stable configuration. All of the polymorphs are wide band gap semiconductors, transparent in the visible region, and with a high refractive index. Recent research is focused on visible photocatalyst, because most of the visible light can not be utilized for photocatalytic reactions of TiO$_2$ as the band-gap energy of TiO$_2$ is approximately 3.2 eV. If the photocatalytic reactions are induced artificially by the irradiation of visible light, the TiO$_2$ becomes efficient and it may contribute to reduce harmful molecules in indoors without UV light source. Conventional metal sulfides and metal calcogenides are photcatalytic materials working with visible light, most of them include toxic elements and they are unstable under light irradiation in a solution or acids. Among various photocatalysts, TiO$_2$ seem to be the most promising material due to its strong oxidizing ability, nontoxicity and long term stability.

![Figure 1.6](image_path)

Figure 1.6 Different phases of TiO$_2$ (a) rutile (b) anatase (c) brookite
1.4 PREPARATION TECHNIQUES

1.4.1 Sol-gel Method

The sol-gel method is a wet-chemical synthesis technique widely used for the preparation of oxide gels, glasses, thin films and ceramic materials at low temperature. The sol-gel process, as the name implies, involves transition from a liquid ‘sol’ (colloidal solution) into a ‘gel’ phase (Wright and Sommerdijk 2001). A sol is a dispersion of the solid particles of size ~ 0.1 - 1 µm in a liquid where there is only the Brownian motions of suspended particles. A gel is a state where the solid network contains liquid components (Brinker and Scherer 1990). Usually inorganic metal salts or metal alkoxides are used as precursors for producing metal oxide thin films. The sol-gel process can be described by the hydrolysis, alcohol and water condensation and polymerization. Ceramic oxide films can be formed by spin, dip or spray coating techniques using sol-gel method. Figure 1.7 shows the flow chart of the materials derived from sol-gel method.

1.4.2 Advantages and limitations of Sol-gel Method

Sol-gel method is a versatile method useful for preparing metal oxides. Stoichiometrical homogeneous control of the doping is easily achieved, since liquid precursors are used, it is possible to cast the glass and ceramics in a range of shapes, such as thin film, fibers, and monoliths, etc, without the need for machining or melting. The precursors such as metal alkoxides, with very high purity make it easy to fabricate materials with high quality and cost effective and the temperature required in the process is low and no delicate vacuum system is needed.
Despite its advantages, sol-gel method still has some limitation. Sol-gel technique is not widely used in industries due to weak bonding, low wear-resistance, high permeability and difficulty in controlling the porosity. Very careful attentions are needed to avoid cracking of the thin films. The trapped organics with the thick coating often result in failure during thermal process. The present sol-gel technique is very substrate-dependent, and the thermal expansion mismatch limits the wide application of sol-gel technique.

1.4.3 Spin Coating Technique

The spin coating process can be broken down into the four stages shown in Figure 1.8. The deposition, spin up, and spin off stages occur sequentially while the evaporation stage occurs throughout the process.

The spin coating process involves, dispense of an excessive amount of sol onto a stationary or slowly spinning substrate. The sol is deposited through a nozzle at the center of the substrate. An excessive amount of sol is used to prevent the discontinuities coating in the edge.

In the spin up stage, substrate is accelerated to the final spin speed. As rotational forces increase, the sol is pulled upward and a wave front is formed. But in substrate edge fairly uniform layer is formed due to the centrifugal force.

The spin off stage is the spin coating stage where the excess solvent is flung off the substrate surface as it rotates at speeds between 2000 and 8000 RPMs. The sol is being thinned primarily by centrifugal forces until enough solvent has been removed to increase viscosity to a level where flow ceases. The spin off stage takes place for approximately 10 seconds after spin up (Carcano et al 1993).
Figure 1.7 Flow chart of materials derived from sol-gel process

Figure 1.8 The Four Stages of the Spin Coating Process (Bornside et al 1987)
Evaporation is the complex process by which a portion of the excess solvent is absorbed into the atmosphere. If significant evaporation occurs prematurely, a solid layer forms on the fluid surface which impedes the evaporation of solvent trapped under this layer and, when subjected to the centrifugal forces of the spinning substrate, causes coating defects.

Spin coating has many advantages like film thicknesses are easily changed by changing the spin speed, or switching to a different viscosity photoresist and ability to get progressively more uniform as it thin, and if the film ever becomes completely uniform during the coating process, it will remain so for the duration of the process.

Spin coating have few disadvantages like large substrates cannot be spun at a sufficiently high rate in order to allow the film to thin and dry in a timely manner resulting in decreased throughput (Emslie et al 1958). Typical spin coating processes utilize only 2-5 % of the material dispensed onto the substrate, while the remaining 95-98 % is flung off into the coating bowl and disposed.

1.4.4 Spray Pyrolysis

Numerous materials have been prepared in the form of thin films over a century because of their potential technical value and scientific curiosity in their properties and the applications to modern technology. Based on the preparation techniques, it will be divided into two types called physical process and chemical process. The physical process includes the pulsed laser deposition, physical vapour deposition, molecular beam epitaxy and sputtering. The chemical method comprises gas-phase deposition methods and solution techniques and is schematically shown in Figure 1.9. The gas-phase methods are chemical vapour deposition (CVD) (Bryant 1997;
Ghoshtagore 1978) and atomic layer epitaxy (ALE) (Suntola 1992), while spray pyrolysis (Chamberlin and Skarman 1966), sol-gel (Brinker et al 1990), spin- (Chen et al 1993) and dip-coating (Brinker et al 1991) methods employ precursor solutions. Owing to their simplicity and inexpensiveness, chemical techniques have been studied extensively for the preparation of thin films.

Spray pyrolysis has been used to deposit dense films, porous films, and for powder production. Even multilayered films can be easily prepared using this versatile technique. Unlike many other film deposition techniques, spray pyrolysis represents a very simple and relatively cost-effective processing method. It offers an extremely easy technique for preparing films of any composition. Spray pyrolysis does not require high-quality substrates or chemicals. Typical spray pyrolysis equipment consists of an atomizer, precursor solution, substrate heater, and temperature controller. Figure 1.10 shows the schematic diagram of home made spray pyrolysis set up.

**Figure 1.9 Thin film deposition methods via chemical route**
In spray pyrolysis technique, the properties of the films depend upon the substrate temperature and precursor solution. Thin-film deposition using spray pyrolysis can be divided into three main steps: atomization of the precursor solution, transportation of the resultant aerosol, and decomposition of the precursor on the substrate (Perednis and Gauckler 2005). In spray pyrolysis, the key issue is to understand the basic atomization process of the atomization device in use. Depending upon the application of the films one can choose the atomizer. Air blast, ultrasonic, and electrostatic atomizers are normally used in spray pyrolysis technique.

During aerosol transport, it is important that as many droplets as possible are transported to the substrate without forming powder or salt particles. Sears and Michael (1988) investigated the mechanism of SnO₂ film growth. The influence of forces, which determine both the trajectory of the droplets and evaporation were examined and a film growth model was proposed and gravitational, electric, thermophoretic and Stokes forces were
also taken into account. Hsuan-Fu Yu and Wen-Haur Liao (1998) developed a model describing the evaporation of solution droplets before the formation of a solid crust and according to his model the transfer of mass, momentum, temperature outside and around the droplet as well as effects of precursor precipitation were taken into account. The interactions between droplets were ignored. Lenggoro et al (2000) investigated powder production by spray pyrolysis using a temperature-graded laminar flow aerosol reactor and they calculated the evaporation rate and the change of the precursor concentration within the droplets. The predicted numerical simulation results were in good agreement with the experimental results.

Finally in decomposition of the precursor, many processes occur simultaneously when a droplet hits the surface of the substrate: evaporation of residual solvent, spreading of the droplet, and salt decomposition. Many models exist for the decomposition of a precursor and most of the authors suggest that chemical vapour deposition based process gives high quality films by spray pyrolysis. Figure 1.11 shows the decomposition of the precursor when increasing the substrate temperature (Perednis and Gauckler 2005).

Spray pyrolysis is a versatile and effective technique to deposit metal oxide films. The most important parameter is the substrate temperature and if the substrate temperature is high then the films are rougher and more porous. If the temperature is too low, the films will be cracked. Also, the substrate temperature influences the crystallinity, texture, and other physical properties of the deposited films. Another important spray parameter is the precursor solution and it affects the morphology and the properties of the deposited films. In addition, the film morphology and properties can be drastically changed by using various additives in the precursor solution (Perednis and Gauckler 2005).
1.4.5 Pulsed Laser Deposition (PLD)

Pulsed laser deposition (PLD) is for many reasons a versatile technique. In this method the energy source is located outside the chamber and hence the use of high vacuum as well as ambient gas is essential. Combined with a stoichiometry transfer between target and substrate this allows depositing such as, oxides, nitrides, carbides, semiconductors, metals and even polymers or fullerenes can be grown with high deposition rates. In high vacuum, implantation and intermixing effects originating in the deposition of energetic particles lead to the formation of metastable phases, for instance nanocrystalline highly supersaturated solid solutions and amorphous alloys. The preparation in inert gas atmosphere makes it even possible to tune the film properties (stress, texture, reactivity, magnetic properties, etc.) by varying the kinetic energy of the deposited particles. All this makes PLD an alternative deposition technique for the growth of high-quality thin films. Figure 1.12 shows a schematic illustration of an experimental setup.
PLD technique uses high power laser pulses to melt, evaporate and ionize material from the surface of a target. The evaporated material is collected on an appropriately placed substrate upon which it condenses and the thin film grows. During the process, one can control laser energy density and pulse repetition rate for getting good quality films.

Figure 1.12 Experimental setup of Pulsed Laser Deposition Technique

The advantages of PLD technique is that the targets used in PLD are small compared with the large size required for other sputtering techniques, produce multi-layered films of different materials, a fine control of film thickness down to atomic monolayer can be achieved by controlling the number of pulses. One of the most important advantages is that the stoichiometry of the target can be retained in the deposited films. PLD generally can be divided into the following four stages:

1. Interaction between laser radiation and the target
2. Dynamic of the ablation materials
3. Decomposition of the target materials onto the substrate
4. Nucleation and growth of a thin film
In the first stage, pulsed laser beam is focused on a target and the laser beam results in a locally very high energy density on the target surface. The electromagnetic energy is converted into thermal energy via electronic processes, and results in evaporation of the source material (Chrisey and Hubler 1994). This process takes place on a very short timescale, shorter than the laser pulse duration. Extremely high temperatures are reached resulting in high density plasma that starts to expand due to the pressure gradient close to the target surface. The instantaneous ablation rate is highly dependent on the fluences of the laser irradiation on the target. The ablation mechanisms involve many complex physical phenomena such as collision, thermal and electronic excitation, exfoliation and hydrodynamics. Figure 1.13 shows the schematic representation of the laser ablation and Figure 1.14 shows the photograph of observed plume in PLD setup.

In the second stage, the emitted materials (plume) tend to move towards the substrate according to the laws of gas-dynamic and show the forward peaking phenomenon (Namiki et al 1986). The uniformity of the films can be controlled by controlling the laser spot size and the plasma temperature. The target-to-substrate distance is another parameter that governs the angular spread of the ablated materials and Hanabusa (1993) found a mask placed close to the substrate could reduce the spreading.

The third stage is important to determine the quality of thin film. The ejected high-energy species from the target material impinge onto the substrate surface. The mechanism of the interaction is illustrated in the following Figure 1.15. The energetic species sputter some of the surface atoms on the substrate and a collision region is established between the incident flow and the sputtered atoms. Film grows immediately after this thermalized region (collision region) is formed. The region serves as a source for condensation of particles. When the condensation rate is higher than the
rate of particles supplied by the sputtering, thermal equilibrium condition can be reached quickly and film grows on the substrate surface at the expenses of the direct flow of the ablation particles.

Figure 1.13 Principle of laser ablation. Energetic laser pulses hit the target and evaporate material from the surface. The emitted particles condense on the substrate surface

Figure 1.14 Photograph of the plume in PLD setup
Fourth stage of nucleation and growth of crystalline films depends on many parameters such as the density, energy, degree of ionization, and the type of the condensing material, as well as the temperature and the physical-chemical properties of the substrate.

1.5 SCOPE OF THE THESIS

Considering the importance of DMS in interdisciplinary materials science and future spintronics applications, the present thesis is focused on the synthesis and property studies of pure and doped TiO$_2$ and ZnO films. Titanium dioxide (TiO$_2$) systems have received much attention due to the existence of ferromagnetic property at room temperature. Matsumoto et al. (2001) first reported that Co doped TiO$_2$ system shows the ferromagnetic property at room temperature with visible photocatalytic activity. The formation of Co doped TiO$_2$ is reported to be very much dependent on the preparation methods. With this motivation, Co doped TiO$_2$ films were prepared by a non-vacuum approach, the sol-gel process and their structural and optical properties have been studied.
Transition and rare earth metal doped ZnO were predicted as the promising materials for future spintronics devices (Dietl et al 2000; Potzger et al 2006). Recently ZnO based system motivated the research in DMS due to prediction of room temperature ferromagnetism in p-type Mn doped ZnO (Dietl et al 2000). To explore the origin of the ferromagnetism arising due to the valance state of Mn, the Mn doped ZnO was prepared by spray pyrolysis and detailed studies on structural, magnetic and optical properties have been carried out. Ferromagnetism has also been observed in Gd and Nd doped ZnO (Potzger et al 2006, Mariana Ungureanu et al 2007). In the present study Gd and Nd doped ZnO thin films have been prepared by spray pyrolysis and the properties are investigated in detail. It is a challenge to achieve highly conducting transition metal doped ZnO films without degrading their magnetic properties, as substitution of transition metal often leads to an increase in resistivity of films. With this motivation, thin films of Zn$_{0.95}$Mn$_{0.05}$O and Zn$_{0.95}$Co$_{0.05}$O with codoping of Ga were prepared by PLD and their structural, optical and magnetotransport properties have been studied.

The shift heavy ion (SHI) irradiation has been widely used for modifications of physical properties of various materials. In this investigation, Mn doped ZnO films were irradiated with heavy ions like oxygen and nickel and the effect of irradiation on the structural and optical properties.