EFFECT OF SWIFT HEAVY IONS IRRADIATION ON STRUCTURAL, ELECTRICAL AND MAGNETIC PROPERTIES OF MAGNETIC THIN FILM

ABSTRACT OF THE THESIS
SUBMITTED FOR THE AWARD OF THE DEGREE OF
Doctor of Philosophy
IN
APPLIED PHYSICS
BY
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UNDER THE SUPERVISION OF

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DEPARTMENT OF APPLIED PHYSICS
Z.H. COLLEGE OF ENGINEERING AND TECHNOLOGY
ALIGARH MUSLIM UNIVERSITY
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2014
Abstract

Modern materials science, both basic and applied research, relies on the development of new materials as well as the exploitation of known materials in unusual geometries and functionalities. Thin films have been emerging as an important class of nanostructured materials with immense possibilities of tailoring their properties in order to achieve the desired functionality. Magnetic materials in particular provide the underlying science for a number of new technologies. Most of magnetic materials of industrial interests are ferromagnetic materials. Magnetic thin films with high coercivity are intensively investigated, in order to satisfy the demand of ever increasing storage density of magnetic and magneto-optical recording. Among the various magnetic materials, Cobalt ferrite (CoFe₂O₄) thin films have been studied extensively for their unusual magnetic properties such as high coercivity, moderate saturation magnetization (Mₛ), large magnetic anisotropy accompanied by a large anisotropic magnetostriiction. There are also materials like rare-earth compounds, CoPt, FePd etc which possesses high coercivity but compared to other potential candidates, CoFe₂O₄ (CFO) have the advantage of being low cost, excellent chemical stability, and mechanical hardness. Recent studies demonstrated that integrating CFO as a pinning layer in the spin valve architecture can strongly enhance the magnetoresistance effect of the sandwiched structure. The potential applications of CFO films require achieving films with perpendicular magnetic anisotropy and high coercivity on inexpensive substrates at a low temperature. However, the issue is a variety of parameters such as film thickness, crystalline structure, compositions, surface/interface roughness and the presence of defects which strongly affect the properties. Specifically, surface/interface roughness influence and presence of defects. Recently, there are numerous reports cited in the literature about the enhancement of magnetic properties with the presence of defects or imperfections.

Swift heavy ion (SHI) irradiation is a unique and effective tool which is known to generate controlled defects such as structural strain, point/cluster of defects and columnar defects or defect annealing. The advantage of SHI irradiation is that the defects can be locally induced in a controllable manner and so properties can be tuned depending upon the electronic energy loss and fluences.
Abstract

In the present study, we have explored the possibility of engineering various physical properties especially structural, morphological, electrical and magnetic by doping In at Fe site in CFO nanoparticles, fabricating CoFe$_2$O$_4$ thin films using pulsed laser deposition (PLD) and rf sputtering on inexpensive substrates such as quartz and silicon substrates and finally by generating defects with SHI irradiation.

**Chapter 1** covers with the introductory idea about the status of present research work along with the structure of this thesis. A brief overview about the magnetism, types of magnetic materials, crystal structure and magnetism of CFO has been presented. The origins of the magnetic anisotropy, the growth of thin films and the creation of defects by swift heavy ion irradiation have been discussed.

**Chapter 2** deals with the study of experimental techniques utilized in the present research work while processing and characterization of the material related to the structural, electrical and magnetic properties. Citrate-gel route have been elucidated for the synthesis of the nanoparticles and PLD and rf sputtering for fabricating CFO thin films. The principles of characterization techniques which were utilized to characterize the different properties of these materials have been discussed in brief.

**Chapter 3** provides with the synthesis of In doped CFO using citrate-gel method followed by the study of structural, electrical and magnetic properties. In this chapter, comparative study of CoFe$_2$O$_4$ and 15 % In doping at the Fe site i.e. Co$_2$In$_{0.15}$Fe$_{1.85}$O$_4$ systems with respect to magnetic, the electrical and dielectric properties is discussed. A considerable change in the magnetization, coercivity, resistivity and dielectric has been observed with In doping.

**Chapter 4** describes the growth of CFO thin films by PLD and rf sputtering on quartz and Si substrates at various depositions conditions. Thin films of different orientations, morphology and thickness were obtained. It is observed that the smooth and flat surface films possess perpendicular magnetic anisotropy (PMA) while the film possessing highest surface roughness shows in-plane anisotropy. The surface roughness of the thin films also affects the electron transport properties.
Abstract

Chapter 5 deals with the study of ion irradiation effect using 200 MeV Ag$^{+17}$ ions at various fluences on CFO films grown by PLD. Structural study by X-ray diffraction (XRD) and Raman Spectroscopy confirms the amorphization and reduction of strain. Room temperature hysteresis loops illustrate PMA in the pristine samples. The anisotropy energy increases at a fluence of $5 \times 10^{11}$ ions/cm$^2$ but the anisotropy ceases and becomes isotropic at fluence $5 \times 10^{12}$ ions/cm$^2$. XRD, Raman spectroscopy, Transmission electron microscope (TEM) and Co L$_{2,3}$ edges XAS and XMCD demonstrate that anisotropic to isotropic transition is brought by modification in structure and strain. Not only the magnetic properties but electrical resistivity is also modified as defects act as scattering sites for charge carriers. In this chapter, thickness dependence of 200 MeV Ag$^{+17}$ ions irradiation at fluences $5 \times 10^{12}$ ions/cm$^2$ also studied and observed that thinner film has been less affected by 200 MeV Ag$^{+17}$ ions irradiation.

Chapter 6 deals with the effect of 200 MeV Ag$^{+17}$ and 100 MeV O$^{+7}$ ions irradiation at various fluences on CFO films grown by rf sputtering to understand the role of ion species and energy. XRD and Raman spectroscopy revealed the partial amorphization of the CFO thin films when irradiated with 200 MeV Ag$^{+17}$ ions while the surface morphology study uncovers the severe effect on the surface of the film when irradiated with 100 MeV O$^{+7}$ ions. This is due to the difference in the electronic energy loss, $S_e$ of the two ion beams. Magnetization study illustrate anisotropic to isotropic transition after the 200 MeV Ag$^{+17}$ ions irradiation at fluences $5 \times 10^{12}$ ions/cm$^2$ and reorientation of anisotropy from PMA to in-plane anisotropy in 100 MeV O$^{+7}$ ions irradiated at a fluence $5 \times 10^{11}$ ions/cm$^2$. This modification is mediated by the modifications of surface morphology.

Chapter 7 summarizes the significant results obtained from the work carried out in this thesis and scope for future work.
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ALIGARH MUSLIM UNIVERSITY
ALIGARH (INDIA)
2014
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TO

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AND
BROTHERS
CERTIFICATE

This is to certify that the thesis entitled "Effect of Swift Heavy Ions Irradiation on Structural, Electrical and Magnetic Properties of Magnetic Thin Film", which is submitted by Razia Nongjai bearing En. No.: GD-5973 for the award of the degree of Doctor of Philosophy in Applied Physics is a record of the bonafide research work carried out by her. She has worked under our guidance and supervision, and has fulfilled the requirements for the submission of the thesis.

The results presented in this thesis have not been submitted in part or in full, to any other University or Institution for the award of any degree or diploma.

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CANDIDATE’S DECLARATION

I, Razia Nongjai, Department of Applied Physics certify that the work embodied in this Ph.D thesis is my own bonafide work carried out by me under the supervision of Dr. Shakeel Khan and co-supervision of Dr. K. Asokan at Aligarh Muslim University, Aligarh. The matter embodied in this Ph.D thesis has not been submitted for the award of any other degree.

I declare that I have faithfully acknowledged, given credit to and referred to the research workers wherever their works have been cited in the text and the body of the thesis. I further certify that I have not willfully lifted up some other's work, para, text, data, result, etc. reported in the journals, books, magazines, reports, dissertations, theses, etc., or available at web-sites and included them in this Ph.D. thesis and cited as my own work.

Date: 5. 11. 2014

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Chapter 1

Introduction

This chapter presents the background for this research work, an overview of magnetism, brief description of the CoFe$_2$O$_4$ material, magnetic anisotropy and growth of thin films and modification of properties by ion irradiation are discussed. Apart from this, the structure of this thesis is also outlined.
1.1 Introduction:

Modern materials science, both basic and applied research, relies on the development of new materials as well as the exploitation of known materials in unusual geometries and functionalities. Thin films have been emerging as an important class of nanostructured materials with immense possibilities of tailoring their properties in order to achieve the desired functionality [1-8]. Magnetic materials in particular provide the underlying science for a number of new technologies. Thin films, layered or pattern structure of magnetic materials are fascinating topic of research and has received a rapidly growing interest due to continuous discoveries of new magnetic phenomena and their increased area of application in advanced technologies [9-16]. Even though enormous progress has been achieved, the area of magnetic thin films is still in the stage of infancy [17]. In the last quarter of the twentieth century, with the information revolution and the ever growing need to acquire, store and retrieve information, the science and technologies attached to magnetic recording have experienced an explosive growth. Central to those pursuits has been the magnetism in materials as it applies to surface, interfaces and thin films [17]. With the discovery of giant magneto-resistance (GMR) the field of data storage has been revolutionized, the size of the read head was reduced to nano-dimensions. This has helped in the areal density of present day products to reach 400 Gbits/in² and led to decrease in the cost per unit of storage [18, 19]. Nonetheless, the pursuit of higher areal densities still continues. The demands for miniaturizing devices require improvement in various properties like electrical, magnetic, optical, mechanical etc and their tuning which would results in improvement in efficiency of the devices.

In order to match the GMR based read heads, the recording medium with optimized magnetic properties such as high coercivity, moderate saturation magnetization ($M_{sat}$) and large magnetic anisotropy are desired. A careful balance is required to keep the anisotropy high enough so that the recorded bits are stable against thermal demagnetization but low enough so that bits can be written with the available field from the write head, while the level of magnetization is high enough so that the recorded bits can be reliably read with the available head technology [19]. The earliest disk drives used $\gamma$-Fe$_2$O$_3$ particles borrowed directly from the technology of magnetic
tape. A variety of other materials has been used, including both crystalline and amorphous metallic layers, mostly based on cobalt because of its relatively high magnetization, high anisotropy and good corrosion resistance.

1.2 Magnetism overview:

The magnetism in materials is due to the unpaired electrons of the atoms which lead to a magnetic moment. Each unpaired spin produces 1 Bohr Magneton ($\mu_B$). In compounds, ions and molecules, account must be taken of the electrons used for bonding or transferred in ionization. It is the number of unpaired electrons remaining after these processes occur that gives the net magnetic moment. Depending upon their response to the application of an externally applied magnetic field, magnetism is categorized as diamagnetism, paramagnetism (PM), ferromagnetism (FM), antiferromagnetism (AF) and ferrimagnetism.

1.2.1 Diamagnetism:

Diamagnetism is an inherent property of the orbital motion of the individual electron in a field. It is only observed when the atom does not have a net spin or orbital moment. The orbital motion sets up a field opposite to the applied field even though compensated in a similar manner to the back emf of Lenz's Law. The effect leads to a negative susceptibility or the actual lowering of the net moment in the material as an external field is applied. Diamagnetism is a very weak effect so that even a small trace of paramagnetic impurity can mask out the effect [19].

1.2.2 Paramagnetism:

If an atom has a net magnetic moment, this moment may be partially aligned in the direction of an applied magnetic field. But in the absence of an external field, the orientation of these magnetic moments is random. Each atom therefore acts as an individual magnet with no mutual interaction in a field. The process of rotating these moments against thermal agitation is a difficult one and a large field is necessary to achieve only a small degree of alignment or magnetization. As the temperature is raised, the thermal agitations of the spins can even destroy this small amount of alignment.
In general, paramagnetic effects are quite small: the magnetic susceptibility is of the order of $10^{-6}$ to $10^{-4}$ of most paramagnets, but may be as high as $10^{-1}$ for synthetic paramagnets such as ferrofluids [20].

1.2.3 Ferromagnetism:

A ferromagnetic material, like a paramagnetic substance, has unpaired electrons. However, in addition to intrinsic magnetic moment of electrons tendency to align parallel to the applied field, there is also a tendency of these magnetic moments to orient parallel to each other through exchange interaction to maintain a lowered-energy state in a region called a domain. Thus, even in the absence of an applied field, the magnetic moments of the electrons in the material spontaneously line up parallel to one another resulting in net spontaneous magnetization. Ferromagnetism is strongly temperature dependent and every ferromagnetic substance has its own individual characteristic temperature, called the Curie temperature or Curie point ($T_C$), above which it loses its ferromagnetic properties. This is because the thermal tendency to disorder overwhelms the energy-lowering due to ferromagnetic order [19].

1.2.4 Antiferromagnetism:

In an antiferromagnet, unlike a ferromagnet, there is a tendency for the intrinsic magnetic moments of neighboring electrons to align but in opposite directions meaning that the exchange interaction is negative. When all atoms are arranged in a substance so that each neighbor is ‘anti-aligned’, the substance is antiferromagnetic. Antiferromagnets have a zero net magnetic moment, meaning no field is produced by them. Like ferromagnetism this ordering is also temperature dependent and vanishes above a critical temperature called the Neel temperature ($T_N$) [19].

1.2.5 Ferrimagnetism:

In Ferrimagnetism, like antiferromagnetism, neighboring pairs of electron spins align in opposite directions. But the moments of opposing spins are unequal and so complete cancellation did not occur and a net moment is resulted. The interactions of the net moments of the lattice are continuous throughout the rest of the crystal so
that ferrimagnetism can be treated as a special case of ferromagnetism and thus domains can form in a similar manner. Ferrimagnets retain their magnetization in the absence of a field and also have a Curie point and one would expect the same type of paramagnetic behavior above the Curie temperature [19].

1.2.6 Magnetic parameters:

Magnetic materials exhibiting ferromagnetic and ferrimagnetic nature are commercially important. The important magnetic parameters can be obtained from the M versus H hysteresis loop. The formation of hysteresis loop is shown in Figure 1.1. The coercivity ($H_c$) is the reverse field that reduces M to zero from saturation magnetization ($M_s$). The remanant magnetization ($M_r$) is the value of M at H = 0. Magnetic memory devices should have high $H_c$ and squareness ($M_r/M_s$) to ensure that a majority of domains have similar switching fields.

![Hysteresis Loop Diagram]

Figure 1.1: Typical hysteresis loop and magnetic domain morphology of ferromagnetic materials [21].
1.3 Magnetic material – \(\text{CoFe}_2\text{O}_4\):

Among the various magnetic materials, Cobalt ferrite \((\text{CoFe}_2\text{O}_4)\) thin films have been studied extensively for their unusual magnetic properties such as high coercivity, moderate saturation magnetization \(M_s\), large magnetic anisotropy and magnetostriction. There are also material like rare-earth compounds, \(\text{CoPt}, \text{FePt}\) etc which possesses high coercivity but compared to other potential candidates, \(\text{CoFe}_2\text{O}_4\) has the advantage of being low cost, excellent chemical stability and mechanical hardness [22-25]. The unique magnetic properties can be understood from its electronic and structural properties.

1.3.1 Structure of \(\text{CoFe}_2\text{O}_4\):

\(\text{CoFe}_2\text{O}_4\) (CFO) is a spinel ferrite and it has a structure derived from mineral spinel, \(\text{MgO.Al}_2\text{O}_3\). The unit cell of the spinel structure is illustrated in figure 1.2. There are eight formula units per cubic unit cell, each of which consists of 32 anions and 24 cations with a total of 56 atoms [19, 26]. The large \(\text{O}^{2-}\) ions (radius about 0.13 nm) are packed quite close together in a face-centered cubic arrangement, and the much smaller \(\text{Fe}^{3+}\) and \(\text{Co}^{3+}\) metals ions (radii from about 0.07 to 0.08 nm) occupy the spaces between them. These spaces are of two kinds. One is called a tetrahedral or A-site, because it is located at the center of a tetrahedron whose corners are occupied by oxygen ions (figure 1.2 a). The other is called an octahedral or B-site, because the oxygen ions around it occupy the corners of an octahedron (figure 1.2 b). The crystallographic environments of the A and B sites are therefore distinctly different. There are 64 tetrahedral interstices (A sites) and 32 octahedral interstices (B sites) exist between the anions. Not all of the available sites are actually occupied by metal ions. Only one-eighth of the A sites and one-half of the B sites are occupied by cations. The cation distribution can be distinctly characterized by the so-called degree of inversion \(\delta\),

\[
(\text{Co}_{1-\delta}\text{Fe}_\delta)_A[\text{Co}_\delta\text{Fe}_{2-\delta}]_B\text{O}_4
\]  

(1.1)

In normal spinels \((\delta = 0)\), the tetrahedral and octahedral sites are occupied by divalent and trivalent cations, respectively, while in the inverse spinels \((\delta = 1)\) all the divalent cations occupy the octahedral sites and trivalent cations occupy tetrahedral and
octahedral sites evenly. When it has partial inverse structure, the spinel is called disordered since the di or trivalent cations may be distributed at both tetrahedral and octahedral sites.

Normally, CFO has an inverse spinel structure, with 8 Co\(^{2+}\) ions occupying half of the octahedral sites, 8 Fe\(^{3+}\) ions occupying the rest of octahedral sites, and the 8 Fe\(^{3+}\) ions in tetrahedral sites. Sometimes, CFO can be a mixed spinel, where the tetrahedral sides are partially occupied by Co\(^{3+}\) ions influenced by heat treatment or chemical environment [25, 27-29]. The site preference of the individual ions for the

Figure 1.2: Crystal structure of spinel ferrite [19].
two types of lattice sites is determined by the ionic radii of the specific ions, the size of the interstices, temperature and the orbital preference for specific coordination. The most important consideration would appear to be the relative size of the ion compared to the size of the lattice site [26, 29]. In CFO, there are six surrounding oxygen ions at the octahedral site, which will have a stronger Coulomb attraction with Fe$^{3+}$ ions than the tetrahedral site with four surrounding oxygen ions. Meanwhile, the interstitial octahedral site has a larger space than that of the tetrahedral site, and thus Co$^{2+}$ ions prefer the octahedral site from the size effect aspect since it has a radius of 0.72 Å, which is greater than that of Fe$^{3+}$ ions, 0.64Å [29.30]. As a result, the site preference will be a competition between the size effect and Coulomb interaction under low temperature, where the entropy contribution is negligible. Hou et al. [29] calculation with various degrees of inversion (x = 0 to 1) indicated that the size effect prevails over the Coulomb effect, as the normal spinel structure is energetically higher than that of the ideal inverse spinel by 0.339 eV/Co. As the temperature increases, the entropy contribution has a remarkable influence on the distribution of Co and Fe ions, as the various partial inverse spinel structures reported in experiments.

1.3.2 Magnetism in CFO:

The magnetic properties of CFO arise from several exchange couplings between the different cations. The magnetic ions Fe$^{3+}$ and Co$^{2+}$ couple by super-exchange interaction via an overlap of their 3$d$ orbitals with the 2$p$ orbitals of an intermediate oxygen anion. The lattice of A ions (A-A) are ferromagnetically coupled in one direction and the lattice of B ions (B-B) in an opposite direction. Thus an antiferromagnetic super-exchange interaction is acting between A-site and B-site ions (A-B). The strength of interaction depends on the distances between these ions and the oxygen ion that links them and also on the angle between the three ions. Figure 1.3 shows the interatomic distances and the angles between the ions for the different types of interactions. In the A-A and B-B cases, the angles are too small or the distances between the metal ions and the oxygen ions are too large. The best combinations of distances and angles are found in the A-B interaction [19, 26]. However, the difference in the magnitude of magnetization of A-site and B-site leads to a net spontaneous magnetization without an external field [31]. Therefore, just as
ferromagnetic, ferrimagnetic materials exhibit substantial spontaneous magnetization at room temperature which makes them industrially important. When the temperature increases, due to the thermal agitation, the arrangement of the spins is disturbed and the net spontaneous magnetization decrease. At a certain temperature, called the Curie temperature \( T_C \), the thermal agitation is strong enough to dominate the exchange force and leads to random arrangement of the spins and the spontaneous magnetization vanishes. Above the Curie temperature, these materials exhibit paramagnetism.

\[ \varphi = 125^\circ 9' \quad 154^\circ 34' \quad 90^\circ \quad 125^\circ 2' \quad 79^\circ 38' \]

<table>
<thead>
<tr>
<th>Distances Me-O</th>
<th>Distances Me-Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>( p = a(\frac{1}{2} - x) )</td>
<td>( b = (a/4)y^2 )</td>
</tr>
<tr>
<td>( q = a(x - \frac{1}{2})/3 )</td>
<td>( c = (a/8)y^3 )</td>
</tr>
<tr>
<td>( r = a(1 + x)/3 )</td>
<td>( d = (a/4)y^3 )</td>
</tr>
<tr>
<td>( r = a(1 + x)/3 )</td>
<td>( e = (3a/8)y^3 )</td>
</tr>
<tr>
<td>( r = a(1 + x)/3 )</td>
<td>( f = (a/9)y^5 )</td>
</tr>
</tbody>
</table>

Figure 1.3: Interionic distances and angles in the spinel structure for the different type of lattice site interactions. [32].

The net magnetic moment is obtained by adding up the interactions between Fe\(^{3+}_A\), Fe\(^{3+}_B\) and Co\(^{2+}\). The Fe\(^{3+}\) and Co\(^{2+}\) ions have five and three unpaired electron in their d-orbitals respectively. The 5 \( \mu_B \) of the Fe\(^{3+}_A\) cations cancel out in the antiferromagnetic A-O-B coupling. Thus, the uncompensated 3 \( \mu_B \) of Co\(^{2+}\) cations determine the moment. Therefore, the calculated saturation magnetization of the complete inverted CFO is 3 \( \mu_B \) per formula unit (f.u) [19, 25]. However, studies have shown that CFO is not perfectly inverse as discussed above, the migration of Co\(^{2+}\) cations
from B to A sites occurs readily, leading to a “mixed” spinel whose μ and electronic band structure may vary significantly from the inverse scenario. Table 1.1 gives the cation distribution and net saturation magnetization per formula unit.

Table 1.1: The cation distribution and net saturation magnetization per formula unit.

<table>
<thead>
<tr>
<th>Structure</th>
<th>A-sites</th>
<th>B-sites</th>
<th>Net moment (μB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fully inverse (Fe)ₐ[CoFe₂]ₜO₄</td>
<td>Fe³⁺(5l)</td>
<td>Fe³⁺(5l)₉,Co²⁺(3l)</td>
<td>3</td>
</tr>
<tr>
<td>Partially inverse (Co₁₋ₐFeₙ)ₐ[Co₈Fe₂₋ₙ]ₜO₄</td>
<td>Fe³⁺(5l)ₙ</td>
<td>Fe³⁺(5l)₉,Co²⁺(3l)ₙ</td>
<td>7 - 4δ</td>
</tr>
</tbody>
</table>

Additionally, Table 1.2 gives a short summary of some physical properties of CFO bulk materials [33].

Table 1.2: Structure and physical properties of CFO.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameter a (Å)</td>
<td>8.38</td>
</tr>
<tr>
<td>Space group</td>
<td>Fd3m (227)</td>
</tr>
<tr>
<td>Curie temperature (°C)</td>
<td>520</td>
</tr>
<tr>
<td>Magnetocrystalline anisotropy constant</td>
<td>2 × 10⁶ ergs/cm³</td>
</tr>
<tr>
<td>Magnetostriiction constants λ</td>
<td></td>
</tr>
<tr>
<td>λ₁₃₁</td>
<td>-200 × 10⁻⁶</td>
</tr>
<tr>
<td>λ₁₃₀</td>
<td>120 × 10⁶</td>
</tr>
<tr>
<td>Stiffness constants (10¹² dynes/cm²)</td>
<td></td>
</tr>
<tr>
<td>C₁₁</td>
<td>2.73</td>
</tr>
<tr>
<td>C₁₂</td>
<td>1.06</td>
</tr>
<tr>
<td>C₄₄</td>
<td>0.97</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>5.29</td>
</tr>
</tbody>
</table>
1.4 Magnetic anisotropy:

Magnetic anisotropy is the directional dependence of magnetic properties. In the absence of an applied field, a magnetically isotropic material has no preferential direction for its magnetic moment, while a magnetically anisotropic material will align its moment with one of the easy axes. An easy axis is an energetically favorable direction of spontaneous magnetization. The direction along which a maximum energy is required to saturate the magnetization is termed as hard axis [19]. This excess energy required to change the orientation of the magnetization from easy to hard axis is termed as the magnetic anisotropy energy ($K_a$). This general subject is of considerable practical interest, because anisotropy is exploited in the design of most magnetic materials of commercial importance. The importance of magnetic anisotropy is well recognised in many technical applications such as permanent magnets or magnetic recording media. A high anisotropy can promote a stable magnetization by pushing down superparamagnetic limit in ultra small nanosized magnetic structures which are needed in advance media for ultrahigh density recording [34]. But minimizing anisotropy is also equally important for technologies that require high susceptibility such as transformers and magnetic inductors [34]. The total magnetic anisotropy is the contribution of many factors. Therefore, a thorough understanding of the sources of anisotropies and their engineering is crucial for the technological applications [19, 34-36].

1.4.1 Origin of magnetic anisotropy:

Magnetic anisotropy has its origin from sample shape, crystal symmetry, stress, or directed atomic pair ordering. Only magnetocrystalline anisotropy is an intrinsic property and reflects the symmetry of the crystals. In reduced symmetry system like thin films, besides crystal anisotropy, extrinsic anisotropy like shape, stress anisotropies are drastically enhanced; competes with each other and may lead to modification or reorientation of anisotropy [31]. Experimentally, it is not always easy to separate these contributions. For films with uniaxial magnetic anisotropy, the overall magnetic anisotropy $K_u$ is usually written as a sum of the various contributions [19].
where $K_{\text{ult}}$ is the intrinsic magnetocrystalline anisotropy, $K_{\text{sh}}$ is the shape anisotropy and $K_{\text{us}}$ is the stress-induced anisotropy.

1.4.2 Magnetocrystalline anisotropy:

Figure 1.4: Magnetization curves for single crystals of (a) iron and (b) nickel [19].

In a crystal lattice, certain crystallographic directions are easier to magnetize compared to other directions and to magnetize in any other directions requires more
energy [19]. Figure 1.4 shows the dependence of magnetization on three important crystallographic axes for iron and nickel. The microscopic origin of magnetocrystalline anisotropy is the spin-orbit coupling. The spins are coupled via the spin-orbit interaction to the orbits which, in turn, are influenced by the crystal lattice. For itinerant materials the spin-orbit interaction induces a small orbital momentum, which then couples the total (spin plus orbital) magnetic moment to the crystal axes. This results in a total energy which depends on the orientation of the magnetization relative to the crystalline axes, and which reflects the symmetry of the crystal. The anisotropy can be described phenomenologically in terms of the direction cosines of the magnetization with respect to rectangular coordinate axes or in terms of spherical harmonics. The magnetocrystalline anisotropy for simple cubic symmetry is given by:

\[
K_{ul} = K_1(a_1^2a_2 + a_2^2a_3 + a_3^2a_1) + K_2a_1^2a_2^2a_3^2
\]  

(1.3)

in terms of the anisotropy constant \( K_{ul} \) and the cosine angles \( \alpha_1, \alpha_2, \alpha_3 \) between the magnetization and the \( a, b, c \)-axes of crystal lattice and \( K_1, K_2 \) are the crystal anisotropy constants.

For hexagonal structures, the anisotropy is said to be uniaxial because there is just one easy axis of magnetization, and so the anisotropy is defined only by the angle of the applied field with the easy axis. The expression for uniaxial anisotropy is

\[
E = K_1 \sin^2 \theta + K_2 \sin^4 \theta + \cdots
\]  

(1.4)

1.4.3 Shape anisotropy:

This anisotropy arises from geometrical shape of the sample [19, 35, 36]. If the sample is spherical then same field magnetize to the same extent in every direction. However, if the sample is not spherical, then it will be easier to magnetize along a long axis than short axis. This is known as shape anisotropy. The origin of shape anisotropy is the anisotropic demagnetizing field. When a sample is magnetized it will produce magnetic charges or poles at the surface. This surface charge distribution is itself another source of a magnetic field which opposes the magnetization that produces it, called the demagnetizing field and is given by:

\[
H_d = -N_d M
\]  

(1.5)
where $M$ is the magnetization vector and $N_d$ is the shape dependent demagnetizing tensor. For a thin film all tensor elements are zero except for the direction perpendicular to the layer: $N_d=1$.

Since the magnetostatic energy can be expressed as:

$$E_d = -\frac{\mu_0}{2V} \int M \cdot H_d \, dV$$  \hspace{1cm} (1.6)

where $\mu_0$ is the permeability of vacuum and $V$ is the volume of the sample, respectively. When the magnetization is saturated and $\theta$ is the angle between the axis normal to the plane of the film and $M$, the average anisotropy energy contribution per unit volume $V$ of a film becomes:

$$E_d = \frac{1}{2} \mu_0 M_s^2 \cos^2 \theta$$  \hspace{1cm} (1.7)

The anisotropy energy is the difference between the magnetostatic energy for the parallel orientation ($\theta = \pi/2$) and the perpendicular orientation ($\theta = 0$), which yields:

$$E_d = \frac{1}{2} \mu_0 M_s^2$$  \hspace{1cm} (1.8)

According to this expression, the contribution favors an in-plane preferential orientation for the magnetization [35].

1.4.4 Stress anisotropy:

Magnetostriction is a well-known phenomenon in magnetic materials by which the change in the magnetization direction induces a dimensional change in a magnetic material. Conversely, the preferred direction of magnetization can be influenced by applying stress through inverse magnetostrictive effect. This effect can also be termed as stress induced magnetic anisotropy. The magnetoelastic energy produced by a stress $\sigma$ is essentially the product of this stress and the resulting value of magnetic strain or magnetostriction $\lambda$. Assuming a uniaxial system, the volume magnetoelastic energy is given by [19, 35]

$$E_{u\sigma} = -\frac{3}{2} \lambda \sigma \cos^2 \theta$$  \hspace{1cm} (1.9)
where $\lambda$ is an isotropic magnetostriction coefficient and $\theta$ is the angle between the magnetization $M$ and $\sigma$. Stress can therefore create uniaxial anisotropy with a stress-induced anisotropy constant given by

$$K_{u\sigma} = -\frac{3}{2} \lambda \sigma$$ (1.10)

Strain in films can be induced by various sources such as intrinsic strain brought about by the nature of the deposition process, the thermal strain associated with differences in thermal expansion coefficients and strain due to non-matching lattice parameters of adjacent layers.

Due to the differences in thermal expansion coefficients, when the substrate-film combination is cooled down to room temperature, an in-plane isotropic tension will be induced in the film. The amount of strain induced due to thermal expansion mismatch can be predicted from [35, 37, 38]

$$\epsilon = (a_s - a_f) \Delta T$$ (1.11)

where $a_s$ and $a_f$ are thermal expansion coefficients of substrate and film, respectively, and $\Delta T$ is the difference between the deposition temperature and measuring temperature usually room temperature.

In thin films strain occurs during growth due to lattice mismatch between layers. The lattice mismatch $\eta$ is given by [34, 35]:

$$\eta = \frac{a_s - a_f}{a_s}$$ (1.12)

where $a_s$ and $a_f$ are lattice constants of the substrate and film respectively. The substrate as well as film will strain to fit each other below a critical thickness if $\eta$ is not too large. The larger lattice spacing will undergo compressive strain and the other will undergo tensile strain. The amount of strain experienced by each layer depends on the ratio of the elastic moduli: the film with the smaller modulus will experience more strain. The relative thickness of the films also contributes to the strain as a thicker film will have more bulk material that favors the bulk lattice spacing at the cost of limiting the flexibility of the interface layer.
1.5 Growth of thin films:

A thin film is defined as a low-dimensional material created by condensing, one-by-one, atomic/molecular/ionic species of matter. The thickness is typically less than one micron. Thin films have very interesting properties that are quite different from those of bulk material. This is because of the fact that their properties depend on a number of interrelated parameters. It is reasonably considered that the thin films may show features that are different from the bulk materials in terms of mechanical strength, carrier transportation, superconductivity, ferroelectricity, magnetic properties, and optical properties. Any thin-film deposition process involves three main steps [38, 39]:

i. Production of the appropriate atomic, molecular, or ionic species.

ii. Transport of these species to the substrate through a medium.

iii. Condensation on the substrate, either directly or via a chemical and/or electrochemical reaction, to form a solid deposit.

Formation of a thin film takes place via nucleation and growth processes. The growth process may be summarized as consisting of a statistical process of nucleation, surface-diffusion controlled growth of the three-dimensional nuclei, and formation of a network structure and its subsequent filling to give a continuous film. Depending on the thermodynamic parameters of the deposit and the substrate surface, the initial nucleation and growth stages may be described as:

(a) *Island type, called Volmer-Weber type.*- Here, the stable nuclei absorb adatoms and grow out in three dimensions. This results in more than one monolayer being completed at the same time and the film continuing to grow in all directions.

(b) *Layer type, called Frank-van der Merwe type.*- In this type, the stable nuclei grow two dimensionally outwards with the addition of adatoms, eventually coalescing and forming a unit cell of thick layer. Once the previous layer is complete then nucleation and growth of the subsequent layer begins.

(c) *Mixed type, called Stranski-Krastanov type.*- Combination of the layer-by-layer mode and island growth modes. Here the film starts with the initial
layers growing in two dimensional mode and at some point after monolayer energy considerations lead to two dimensional mode being unfavorable and three dimensional islands begin to form.

The growth stage of thin films is governed by the surface energy of thin films, \( \gamma_t \), the surface energy of substrates, \( \gamma_s \), and the interfacial energy between thin films and substrates, \( \gamma_h \). The island growth (Volmer-Weber mode) will be predominant at \((\gamma_s - \gamma_h) < \gamma_t\), and the layer growth (Frank-van der Merwe mode) at \((\gamma_s - \gamma_h) > \gamma_t\).

1.5.1 Structural consequences of the growth process:

The microstructure and topographical details of a thin film of a given material depend on the kinetics of growth and hence on the substrate temperature, the source and energy of impurity species, the chemical nature, the topography of the substrate, and gas ambient. These energy of the incident species, deposition rate, supersaturation (i.e., the value of the vapor pressure/solution concentration above that required for condensation into the solid phase under thermodynamical equilibrium conditions), the condensation or sticking coefficient (i.e., the fraction of the total impinging species adsorbed on the substrate), and the level of impurities.

1.5.1.1 Microstructure:

Thin films exhibit a wide variety of microstructures characterized in terms of grain size, lattice defects and surface morphology. The lateral grain size is expected to increase with decreasing supersaturation and increasing surface mobility of the adsorbed species. As a result, deposits with well-defined large grains are formed at high substrate and source temperatures, both of which result in high surface mobility. Increasing the kinetic energy of the incident species (for example, by increasing the source temperature in the case of deposition by vacuum evaporation, or by increasing the sputtering voltage in the case of deposition by sputtering) also increases the surface mobility. However, at sufficiently high kinetic energies, the surface mobility is reduced due to the penetration of the incident species into the substrate, resulting in a smaller grain size. This effect of the kinetic energy of the impinging species on grain size is more pronounced at high substrate temperatures. Also, the effect of substrate temperature on grain size is more prominent for relatively thicker films. The
surface mobility of the adsorbed species may be inhibited, for example, by decreasing the substrate temperature, by introducing reactive impurities into the film during growth, or by co-depositing materials of different atomic sizes and low surface mobility. Under these conditions, the film is amorphous-like and grows layer-by-layer.

Giving the film a post-deposition annealing treatment at temperatures higher than the deposition temperature may also modify the grain size. The higher the annealing temperature, the larger the grain sizes obtained. The effect of heat treatment is again more pronounced for relatively thicker films. The grain growth obtained during post-deposition annealing is significantly reduced from that obtained by depositing the film at annealing temperatures; this is because of the involvement of the high activation-energy process of thermal diffusion of the condensate atoms in the former case compared to the process of condensation of mobile species in the latter.

For a given material-substrate combination and under a given set of deposition conditions, the grain size of the film increases as its thickness increases. However, beyond a certain thickness, the grain size remains constant, suggesting that coherent growth with the underlying grains does not go on forever, and fresh grains are nucleated on top of the old ones above this thickness. This effect of increasing grain size with thickness is more prominent at high substrate temperatures. The effect of various deposition parameters on the grain size is summarized qualitatively in figure 1.5. It is clear that the grain size cannot be increased indefinitely because of the limitation on the surface mobility of the adsorbed species.

Under conditions of a low nucleation barrier and high supersaturation, the initial nucleation density is high and the size of the critical nucleus is small. This results in fine-grained, smooth deposits which become continuous at small thicknesses. On the other hand, when the nucleation barrier is large and the supersaturation is low, large but few nuclei are formed, resulting in coarse-grained rough films which become continuous at relatively large thicknesses. High surface mobility, in general, increases the surface smoothness of the films by filling in the concavities. Surface roughness is also essentially related to the modes of film growth described earlier in section 1.5. The Frank-van der Merwe mode provides the smooth
surface and Volmer-Weber mode provides the rough surface. The strains due to the thermal expansion mismatch between a film and its substrate affect the surface microstructure and/or the roughness [40].

Figure 1.5: Qualitative representation of the influence of various deposition parameters on the grain size of thin films [39].

1.5.1.2 Texture evolution:

With the grain growth in films, the crystallographic orientation of different grains may be randomly distributed as in case of polycrystalline films or the films may be textured through the preferential growth of grains with particular crystallographic orientations. One aspect of energetics of texture formation is minimization of surface and interface energy; another important aspect of the energetics of grain growth in thin films is that they are often under high intrinsic or extrinsic stresses [41]. In continuous films, these strains are largely biaxial, thus the associated strain energy density in different grains is given by

-19-
\[ E_e = \varepsilon^2 M_{hkl} \]  

(1.13)

where \( \varepsilon \) is the strain and \( M_{hkl} \) the effective biaxial modulus. \( M_{hkl} \) depends on the crystallographic direction \( (hkl) \), which is normal to the plane of the film and therefore normal to the plane of the strain. The biaxial modulus for grains with arbitrary \( (hkl) \) texture can be calculated using equations given in [42].

In terms of energy minimization, surface and interface energy minimization and strain energy minimization compete in defining the texture during grain growth. The average driving force arising from surface and interface energy minimization is

\[ F_{s/i} = \frac{\Delta \gamma_1 + \Delta \gamma_i}{h} \]  

(1.14)

Where \( \Delta \gamma_i \) is the difference in the average surface energy of the film and the minimum surface energy, \( \Delta \gamma_i \) is similarly defined for the interfacial energy and \( h \) is the film thickness. It is thought that for polycrystalline films on amorphous substrates, interface energy minimization does not favor growth of grain with specific in-plane orientation. However, for polycrystalline films on single-crystal substrates or textured underlayers, \( \Delta \gamma_i \) depends on the in-plane orientation of the grain, and grain growth is expected for films composed of grain with three-dimensionally constrained or epitaxial orientations.

The average driving force arising from strain energy density minimization is

\[ F_e = \varepsilon^2 \Delta M \]  

(1.15)

where \( \Delta M \) is the difference in the average biaxial modulus of the film and the minimum modulus. A transition in dominant texture will occur when \( F_{s/i} = F_e \), with surface and interface energy minimization dominating when \( F_{s/i} > F_e \), i.e. in films with low \( h \) and \( \varepsilon \), and strain energy minimization dominating when \( F_{s/i} < F_e \), i.e. in thicker films with higher elastically accommodated strains. One way in which \( \varepsilon \) can be varied at the temperature at which grain growth occurs is to vary the deposition temperature, \( T_{dep} \), so that strain energy minimizing textures are expected to be favored during grain growth of films which are deposited at low temperatures. In sufficiently
thin films surface and interface energy minimizing textures are favored, regardless of
their strain or thermal history.

1.5.1.3 Strain formation in thin films:

Strain \( \varepsilon \) in thin films can be introduced during and after fabrication of thin
films. These are established when the constraint of the substrate forces the atoms in
the film to maintain a spacing different from their equilibrium positions under the
ambient conditions [23, 24]. The different type of strain and its calculation are
discussed in section 1.4.4.

1.6 Ion irradiation of material:

Energetic ions passing through materials are known to modify the mechanical,
electrical, optical, magnetic and superconducting properties of the target material by
defect annealing, cluster of point defects and columnar type of defects depending on
the mass and energy of the ion and the material [43, 44]. Therefore it can be used to
engineer the desired properties in a material. The energetic ion during their passage
through a material, energy is transferred to the lattice of the target material via two
processes: nuclear energy loss \( S_n \) and electronic energy loss \( S_e \) [43, 45]. In the former
process, the energy is lost by elastic collisions of incident ions with the atoms in the
material, which is dominant at low energies. In the electronic energy loss process, the
energy is lost by inelastic collisions of the ion with the atoms, leading to excitation or
ionization of the atoms and is dominant at high energies (>1 MeV/nucleon). At these
energies of heavy ions, the velocity of the ion is comparable to or higher than the
velocity of Bohr electron. The ions with such high energies are also referred to as
swift heavy ions (SHI). The electronic energy loss for SHI is, generally, about two
orders of magnitude higher than the nuclear energy. The ion mass and its energy,
decide the magnitudes of the electronic as well as nuclear energy losses. Especially
for heavy ions at high energies (i.e., for SHI), the electronic energy loss decides the
type of defects as the nuclear energy loss is insignificant.
Kinematics describing the collision of two particles in $S_e$ is determined by the law of conservation of energy and momentum. The energy-loss rate, $dE/dx$, may be calculated using computer program “Stopping and ion ranges in matter (SRIM)” code. For projectile particles with energy of the order of MeV per nucleon (MeV/n), the electronic energy loss dominates. As an example, figure 1.6 shows the calculations performed for Ag ions in CFO from energy range of 10 keV to 1 GeV. The vertical line marks 200 MeV of the incident ion energy, the value of nuclear and electronic energy losses at 200 MeV for Ag in CFO are 2059 and 5.551 eV/Angstrom respectively. From these values, it can be seen that at higher energies, the electronic energy loss dominates over nuclear energy loss and at energy of few hundreds of keV, the opposite is true. For a target that contains more than one element, Bragg’s rule is used, which states that the energy loss for a compound is the sum of the losses of the constituent elements. It is seen that in most materials, when the electronic energy loss is more than a certain threshold value (characteristic of that material), then amorphized regions develop along the path of the incident ions. These amorphized
regions are called tracks. The emergence of these tracks results from the local electronic energy deposition along the ion path. Two basic models of microscopic energy transfer mechanism are described below [46, 47].

1.6.1 Coulomb explosion model:

![Diagram of Coulomb explosion model]

Figure 1.7: Schematic of the cylindrical path around the passage of the incident ion according to the coulomb explosion model.

According to this model, during the passage of SHI through materials, positive ions are produced by electronic excitation induced ionization along the projectile-ion trajectory. The rate of ionization per unit path length of ion is denoted by \( \frac{\partial J}{\partial x} \) and it is first calculated by Bethe,

\[
\frac{\partial J}{\partial x} = \frac{A Z^2_e \ln(B E_m)}{E_m}
\]  

(1.16)

where \( A \) and \( B \) are constants which depend on the incident ion and target material, \( Z_{eq} \) is the equilibrated charge of the ion and \( E_m \) is energy of ion per unit atomic mass, \( ln \) is natural logarithm function. As a result of the primary ionization, an ion cloud along the projectile trajectory is formed [48]. These positive ions are mutually repulsive.
The time to cover atomic sites is short in comparison to the response time of the conduction electrons. So during the passage of the ion a long cylinder containing charged ions is produced (figure 1.7). This cylinder containing the charged ions explodes radially due to conversion of electrostatic energy to coherent radial atomic movements under coulomb forces until ions are screened by conduction electrons. Due to the resulting cylindrical shock wave, ion tracks may be formed along the trajectory of the ion due to radial coulomb explosion. This mechanism works well in insulating and semiconducting materials.

1.6.2 Thermal spike model:

![Diagram of amorphous cylindrical ion track with labels](image)

Figure 1.8: Schematic of the amorphous cylindrical ion track around the passage of the incident ion according to the Thermal spike model.

The thermal spike model is the other competing process, which is also responsible for the formation of tracks [45]. According to this model, during the passage of SHI the kinetic energy of the electrons ejected due to inelastic collision induced electronic excitation which is transmitted to the other electrons due to
electron-electron interaction in a time of the order of $10^{-15}$ s. Finally, the energy is transferred to the lattice via the electron-phonon interaction in a time of the order of $10^{-12}$ s leading to large increase of local temperature for a short duration (in ps). An increase of the lattice temperature is due to a two-step process [49, 50, 51]:

i) Thermalization of the deposited energy on the electron system via electron-electron interaction and

ii) Transfer of this energy to the lattice via electron-atom interaction.

As the electron and atom systems are not in thermal equilibrium with each other, the space and time evolutions of electronic system and lattice temperatures, $T_e$ and $T$ respectively, are governed by a set of coupled nonlinear differential equations. As radiation defects created in materials by highly energetic ions are cylindrical [52], a time-dependent thermal transient process is expressed in cylindrical geometry:

\[
\rho C_e(T_e) \frac{\partial T_e}{\partial t} = \frac{\delta}{\delta r} \left[ K_e(T_e) \frac{\partial T_e}{\partial r} \right] + \frac{K_e(T_e)}{\tau} \frac{\partial T_e}{\partial r} - g(T_e - T) + A(r) \quad (1.17)
\]

\[
\rho C(T) \frac{\partial T}{\partial t} = \frac{\delta}{\delta r} \left[ K(T) \frac{\partial T}{\partial r} \right] + \frac{K(T)}{\tau} \frac{\partial T}{\partial r} + g(T_e - T) \quad (1.18)
\]

where $C_e$, $C$ and $K_e$, $K$ are the specific heat and thermal conductivity for the electronic system and lattice, respectively, $\rho$ is the material density, $A(r)$ is the energy brought on the electronic system in a time $t$ considerably less than the electronic thermalization time and $r$ is the radius in cylindrical geometry with the heavy ion path as the axis. $A(r)$ can define as \( \int \int 2\pi r A(r,t) \, dr \, dt = S_e \). The electron-phonon coupling factor $g$ is given by:

\[
g = \frac{\pi^4 (K_B n_e s)^2}{18 K_e(T_e)} \quad (1.19)
\]

where $K_B$ is the Boltzmann’s constant, $n_e$ is the electron density and $s$ is the speed of sound in the metal.

Above a certain $S_e$ threshold, this lattice temperature may exceed the melting temperature of the lattice within a cylinder of radius i.e. latent track, of the order of a few nm. After that time both temperatures decrease and are governed by the thermal conductivity. The rapid quenching ($10^{13}-10^{14}$ K/s) of the molten phase results in an amorphous linear structure when solidifies. Figure 1.8 shows the schematic of the
amorphous cylindrical ion track around the passage of the incident ion. This model has been used to describe the track formation in many materials like insulators [53], semiconductors [49] and metals [50].

1.7 Aim of the thesis:

CoFe$_2$O$_4$ (CFO) has attracted much attention in recent years as one of the potential materials for high density magnetic and magneto-optical recording media because of their unique physical properties. The properties of these material is influence by many factors such as compositions, microstructures, size and geometry, processing temperature, presence of impurity, defects and strain etc. Present thesis focuses on the studies of effect of doping in CFO, the growth of thin films of CFO, the effect of ion irradiation (SII) induced modifications in structural, magnetic and electrical properties. This has been carried out through three main steps:

I. Studying the chemical doping effect by synthesizing CoIn$_x$Fe$_{3-x}$O$_4$ (x=0, 0.15) nanomaterial and characterizing them for structural, magnetic and electrical properties (chapter 3).

II. Growing thin films of CFO with different orientation and thickness, and to investigate the relationship between structures, magnetic and electrical properties of the grown films (chapter 4).

III. Finally, exploring the effect of presence of defects in CFO thin films created by swift heavy ion irradiations on the structural, magnetic and electrical properties (Chapter 5 & 6).
References:


Chapter 2

Experimental Techniques

In this chapter, the experimental techniques including thin film deposition, structural, electrical and magnetic properties characterizations used in the present work are briefly described.
2.1 Synthesis:

2.1.1 Nanoparticles and target material:

There are various methods available for synthesis of powder material or precursor such as solid state reaction, ball-milling, sol-gel, co-precipitation, micellar method, hydrothermal method etc [1-3]. Among these, the sol-gel method is one of the versatile techniques that have advantage of homogenous mixing of the component at molecular level and also simple, and cost-effective without involvement of sophisticated devices. In the present work, ferrites of composition CoIn_xFe_{2-x}O_4(x=0, 0.15) were prepared by sol-gel method.

The starting solutions were prepared by dissolving stoichiometric amount of nitrates of Iron, Cobalt, Indium and citric acid into deionized water to form mixed solution. The molar ratio of nitrates to citric acid was 1:1. The mixed solution were heated at 80°C under constant stirring on the magnetic stirrer to allow evaporation until the reddish brown transparent liquid converted into gel, containing all cations homogeneously mixed together at atomic level. As there was no precipitation at any stage, the problem of segregation of phases, which normally occur in some other chemical methods, did not occur in this material. These gels were heated at 100°C for 24 h in an oven to form loose fluffy powder. The powder was grinded for half an hour and sintered at 600°C for 6 hrs and again grinded for half an hour [4].

To make dense and hard target for thin film deposition, powder was pressed into pellets under a pressure of 4 tons (1 ton = 1.016 x 10^3 kg). The pellet was sintered at 1200°C at a heating rate of 3°C min⁻¹ in a programmable furnace and was subsequently cooled to room temperature at the same rate.

2.1.2 Thin film deposition:

Deposition techniques fall into two broad categories (i) physical vapor deposition (PVD) and (ii) chemical vapor deposition (CVD), depending on the process whether the process is primarily physical or chemical [5]. In both cases, the techniques are based in the formation of vapor of the material to be deposited, so that the vapor is condensed on the substrate surface as a thin film. In PVD, the solid material is converted into vapor through heating (evaporation) or energetic ion
bombardment whereas in CVD usually the process must be performed in vacuum or in controlled atmosphere, to avoid interaction between vapor and air. The various deposition processes which are under these two broad categories are shown in figure 2.1.

![Diagram of Thin Film Deposition Processes]

Figure 2.1: Thin film deposition processes [5].

In the present work, thin films of CFO were deposited on the quartz and Si (100) substrate using the techniques of pulsed laser deposition (PLD) and rf sputtering.

2.1.2.1 Pulsed laser deposition:

Pulsed laser deposition (PLD) is a well-established technique for growing high-quality thin films of alloys and/or compounds with a controlled chemical composition [5]. In this technique, a high-power laser (10⁶-10⁸ W) is irradiated onto the surface of the target materials. The incident laser is in the form of pulses of typical duration of 20 ns. These lasers generate non-equilibrium evaporation leading to the congruent evaporation of target material because it penetrates only a thin surface layer on the target for a few tens of nanoseconds. A typical set-up for PLD is as shown in figure 2.2. A KrF excimer laser (Lamda Physik Compex LPX200), operating at a wavelength of 248 nm and pulsed duration of about 20 ns is focused on the target using a quartz lens to increase the energy density of the laser power on the target.
source. The target is put in UHV chamber where the beam is incident on it at an angle of 45°. The target was mounted on the rotating target holder. A small DC motor was used to rotate the target. The substrate was mounted in front and parallel to the target at a distance of 4-5 cm on a resistive heater with the help of thin conducting silver layer or clamp. The heater could go up to temperature of 850 C. The temperature of the substrate could be measured using a calibrated thermocouple placed on the substrate or on separate small piece of substrate itself.

PLD is often described as a three-step process consisting of (i) laser-target interaction and vaporization of a target material, (ii) plasma plume formation and its transport towards the substrate, and (iii) nucleation of the ablated species and growth of thin film on the substrate surface [6]. When the laser beam strikes the rotating target, the UV laser radiation is absorbed by the outermost layers of the target surface. This causes rapid heating and vaporization of the target material to form dense plasma consisting of excited atoms, molecules, ions and neutral species. The highly energetic ablated species expand perpendicularly to its surface in the form of a luminous plume and travel towards the substrate, crystallizing into a film with a composition typically identical to that of the target material [7].

For depositing good crystalline films, there are various issues which should be taken care of while deposition like background pressure, laser power density, pulsed repetition rate, target to substrate distance. PLD has several characteristics that distinguish it from other film-growth processes and provide special advantages for the growth of oxides and multicomponent materials:

(i) The fact that a laser is used as an external energy source results in an extremely clean process without filaments.

(ii) The stoichiometric transfer of materials under the proper choice of laser fluence films i.e. the deposited film has the same composition as the target.

(iii) Since the deposition chamber does not require any electron beam or hot filament, ambient gases can be used. Energetic species of the ablated plasma react with ambient gas molecules facilitating the deposition of multicomponent ceramic materials.
In spite of these significant advantages, industrial uptake of PLD has been slow and to date most applications have been confined to the research environment for the following reason:

(i) The plasma plume created during the laser ablation process is highly forward directed; therefore the thickness of material collected on a substrate is highly non-uniform across the film. The area of deposited material is typically around 1 cm$^2$.

(ii) The ablated material contains macroscopic globules of molten material, up to ~10 μm diameter. The arrival of these particulates at the substrate is obviously detrimental to the properties of the film being deposited.

In the present study, deposition of CFO thin films was done at UGC-DAE-CSIR Indore center, Indore (M.P), India.

![Diagram of PLD set-up](image)

Figure 2.2: A typical PLD set-up [5].

### 2.1.2.2 Rf sputtering:

Sputtering is a physical vapor deposition (PVD) process used for the deposition of films. It is a process where atoms are ejected from a solid target material due to bombardment of the target by energetic particles and condensing the ejected...
atoms onto a substrate in a high vacuum environment as shown in figure 2.3 [8]. The basic process is as follows: a target, or source of the material desired to be deposited, is bombarded with energetic ions, typically inert gas ions such as Argon (Ar\(^+\)). The collision of these ions onto the target ejects target atoms into the space. These ejected atoms then travel some distance until they reach the substrate and start to condense into a film. As more and more atoms coalesce on the substrate, they begin to bind to each other at the molecular level, forming a tightly bound atomic layer. One or more layers of such atoms can be created at will depending on the sputtering time, allowing
for production of precise layered thin film structures. Several sputtering systems are available for thin-film deposition including dc, rf, magnetron, and ion-beam sputtering. Among these systems, the simplest one is the dc sputtering system. The dc sputtering system is composed of a pair of planar electrodes in which electrons and ions are accelerated by a constant electric field applied between an anode and the cathode. The target is kept at a negative potential (cathode) and the substrate on which film is to be deposited is kept at a positive potential (anode). All type of conducting materials can be deposited by this technique but for insulating target it is not possible because of the immediate buildup of a surface charge of positive ions on the target surface that resists any further ion bombardment on the target.

RF-sputtering system is used for deposition of insulators. The use of radio frequency (RF) generator is essential to maintain the discharge and to avoid charge build-up when sputtering. Generally, 13.56 MHz frequency is used. The most important aspect in this technique is the impedance matching network between power supply and discharge chamber that consists of an LC circuit with variable impedance. The impedance is matched, by varying the impedance of this network to transfer maximum power to the load. Grounding of the substrate is done to avoid the undesirable RF voltages which may develop on the surface. Capacitive coupling is essential for sputtering metals and alloys to sustain the self-biased negative potential. However, if an insulator is to be sputtered, it is not required as the insulator itself serves the purpose of the capacitor [9]. To enhance the ionization rate by emitted secondary electrons even further, a permanent magnet is placed behind the target and is known as a rf-magnetron sputtering system. The schematic of the system set up is shown in figure 2.5. The system consist of three parts: sputtering chamber along with vacuum system, the gas flow system and the RF system with matching network. The sputtering chamber contains a target holder acting as cathode and a substrate holder acting as anode. Substrates are kept on anode at a distance of 3-5 cm from the cathode. The selection of the distance is based on the fact that enough number of collisions should take place in gaseous medium for an operating pressure ($\sim 10^{-2}$ torr). The cathode is connected to RF power supply while anode and rest of the system are properly grounded with metallic strips. The substrate holder is kept on an electrically insulated height adjustable table. It is attached to a heating coil, which acts as a
substrate heater. Variac is connected to this heater to change the current in the heater and thereby the temperature. A thermocouple based temperature sensor is used to read the temperature. Target holder is made up of metal, which is provided with water connections to cool it. A proper RF shielding in the sides of the cathode is done to check the spread of plasma within the cathode and the anode. The gas flow system of the set-up is used to flow the gases required. Ar ions are formed by the impact of electrons under the applied voltage and the required operating pressure is adjusted using the pumping system. In the present work, thin films of CFO were prepared by RF sputtering at IUAC, New Delhi.

Figure 2.5: The schematic of the rf sputtering system.
2.2 Swift heavy ion (SHI) irradiation:

The deposited films were irradiated with swift heavy ion (SHI) using the tandem pelletron accelerator at Inter University Accelerator Centre (IUAC), New Delhi. Pelletron at IUAC is a tandem Van de Graaff accelerator [10] which can accelerate particles from few MeV to hundreds of MeV. Figure 2.6 illustrates the working of the pelletron. In this, negative ions are produced and pre-accelerated to \(~300\) KeV in ion source. The ion beam is selected by injecting magnet, which selects the mass of the ion using mass spectroscopy. The pre-accelerated ions are injected into strong electrical field inside an accelerator tank filled with \(\text{SF}_6\) insulating gas at a pressure of \(~6-7\) atmospheres. The accelerator tank height is 26.5 m with a diameter of 5.5 m. At the centre of the tank, is a terminal shell, which is maintained at a high

![Diagram of IUAC Pelletron](image_url)

Figure 2.6: Schematic of IUAC Pelletron.
voltage (~15 MV). The negative ions on traversing through the accelerating tubes from the column top of the tank to the positive terminal get accelerated. On reaching the terminal these ions pass through a stripper, which removes some electrons from the negative ions, thus transforming the negative ions into positive ions. These positive ions are then repelled away from the positively charged terminal and are accelerated to the ground potential to the bottom of the tank. In this manner, same terminal potential is used twice to accelerate the ions. On exiting from the tank, the ions are bent into horizontal plane by analyzing magnet. The switching magnet diverts the high energy ion beams into various beam lines into the different experimental areas of the beam hall. All the operations for tuning the beam for experiments are done from the control room using computers. The data is collected and the experiment is monitored from the data room adjacent to the control room (for some experiments, data collection is done at some other corresponding places). There are various beamlines at IUAC for studies in materials science, nuclear physics, atomic physics, AMS and radiation biology. In the present study, ion beams of 200 MeV Ag and 100 MeV O ions from IUAC Pelletron in materials science were used.

2.3 Characterizations:

2.3.1 X-ray diffraction:

![Schematic Illustrating XRD Set-up](image)

Figure 2.7: Schematic illustrating XRD set-up.

X-ray diffraction (XRD) is a widely used, simple, versatile, non-destructive technique to identify the crystalline phases present in solid materials and analyze the
structural properties. This is an appropriate technique for both forms of samples i.e. thin film as well as bulk. The instrumentation for X-ray diffraction involves an X-ray source, which provides the incident beam on the sample, and an X-ray detector, which measures the intensity of the diffracted beam emanating from the sample at a certain angle (figure 2.7). Diffraction patterns showing peaks and intensity of various crystallographic textures can then be obtained and analyzed.

![Diagram](image)

Figure 2.8: Schematic representation of Bragg’s condition of x-ray diffraction [11].

The basic principle is based on Bragg's law given by [11]:

\[ 2d \sin \theta = n \lambda \]  

(2.1)

where \( \theta \) is the angle of incidence of the X-rays, \( d \) is the interatomic spacing of the planes, \( \lambda \) is the wavelength of the X-rays, and \( n \) is a positive integer representing the order of the diffraction peak. Figure 2.8 shows an incident beam of parallel X-rays impinging the crystal surface at an angle \( \theta \), and getting reflected from the parallel planes of atoms formed by the crystal plane of the material. Constructive interference of the reflected rays occurs only when their path difference is an integer multiple of the wavelength of X-ray as given in Equation 2.1. By scanning the sample through a range of \( 2\theta \) values a characteristic diffraction pattern is produced and plotted as
intensity (I) versus 2θ graph. The measured pattern can be then compared with a known database of reference patterns to determine the crystal structure of the film.

The peaks in the diffraction pattern acquire a nonzero width due to the instrumental resolution, finite grain size and random strains. A rough estimate of the grain size (d) can be obtained from the XRD pattern using the Scherrer equation,

\[ d = \frac{0.94 \lambda}{\beta \cos \theta} \]  

(2.2)

where β is the full width at half maximum for the diffraction peak at 2θ value. In the present study, the XRD measurements were carried out at IUAC, New Delhi and IUC, Indore using the Bruker D8 Advanced diffractometer with Cu Kα radiation (\( \lambda = 1.542 \) Å).

2.3.2 Raman spectroscopy:

![Diagram of Raman spectroscopy](image)

Figure. 2.9: Schematic showing the different scattering possibilities.

Raman spectroscopy is a spectroscopic technique based on inelastic scattering of monochromatic light, usually from a laser source. When a photon is incident on a solid, the frequency of inelastically scattered photon is shifted above or below the original monochromatic frequency, which is called the Raman effect. This shift provides information about vibrational, rotational and other low frequency transitions.
in molecules, Raman spectroscopy can be used to study solid, liquid and gaseous samples.

The Raman effect is based on molecular deformations in electric field $E$ determined by molecular polarizability $a$. The laser beam can be considered as an oscillating electromagnetic wave with electrical vector $E$. Upon interaction with the sample it induces electric dipole moment $P = aE$ which deforms molecules. Because of periodical deformation, molecules start vibrating with characteristic frequency $\omega_m$. Amplitude of vibration is called a nuclear displacement. In other words, monochromatic laser light with frequency $\omega_0$ excites molecules and transforms them into oscillating dipoles. Such oscillating dipoles emit light of three different frequencies (figure 2.9) when:

(i) A molecule with no Raman-active modes absorbs a photon with the frequency $\omega_0$. The excited molecule returns back to the same basic vibrational state and emits light with the same frequency $\omega_0$ as an excitation source. This type of interaction is called an elastic Rayleigh scattering.

(ii) A photon with frequency $\omega_0$ is absorbed by Raman-active molecule which at the time of interaction is in the basic vibrational state. Part of the photon’s energy is transferred to the Raman-active mode with frequency $\omega_m$ and the resulting frequency of scattered light is reduced to $\omega_0 - \omega_m$. This Raman frequency is called Stokes frequency, or just “Stokes”.

(iii) A photon with frequency $\omega_0$ is absorbed by a Raman-active molecule, which, at the time of interaction, is already in the excited vibrational state. Excessive energy of excited Raman active mode is released, molecule returns to the basic vibrational state and the resulting frequency of scattered light goes up to $\omega_0 + \omega_m$. This Raman frequency is called Anti-Stokes frequency, or just “Anti-Stokes”.

A Raman system typically consists of four major components [12]:

(i) Excitation source (Laser).

(ii) Sample illumination system and light collection optics.

(iii) Wavelength selector (Filter or Spectrophotometer).
(iv) Detector (Photodiode array, CCD or PMT).

The sample is illuminated using monochromatic light from a laser and the scattered light is collected using suitable collection optics. The light is then passed through the spectrometer and the Raman spectra are obtained. In the collected light, the dominant contribution is from Rayleigh scattering. Because of imperfections in the gratings and mirrors within the spectrometer, a portion of the Rayleigh scattered light is present in the Raman spectra in the range of 0 to 200 cm$^{-1}$. Although the fraction of the Rayleigh scattering in this region is very small, it can overshadow the Raman spectra as the intensity of Rayleigh component is very high. Thus the Raman peaks in this region can be observed only when the Rayleigh scattered light is strongly reduced. For this purpose, a notch filter is used; it removes the Rayleigh scattered radiation (as well as Brillouin scattered light and Mie scattering from dust particles).

In this study, the Raman spectra for the samples were recorded at room temperature using Renishaw in Via Raman microscope with Ar ion laser excitation of 514 nm in back scattering geometry, at IUAC, New Delhi.

2.3.3 Scanning electron microscope:

Scanning electron microscope (SEM) is one of the most widely used techniques to characterize the surface morphology of the samples [13]. A schematic of the typical SEM is shown in figure 2.10. Electrons thermionically emitted from a cathode filament are drawn to an anode, focused by two successive condenser lenses into a beam with a very fine spot size (~50 Å) [14]. Pairs of scanning coils located at the objective lens deflect the beam either linearly or in raster fashion over a rectangular area of the specimen surface. Electron beams having energies ranging from a few thousand to 50 keV, with 30 keV a common value, are utilized. Upon impinging on the specimen, the primary electrons decelerate and in losing energy transfer it inelastically to other atomic electrons and to the lattice. Through continuous random scattering events, the primary beam effectively spreads and fills a teardrop-shaped interaction volume which extends from less than 100 nm to approximately 5 μm into the surface. The size of the interaction volume depends on the landing energy
of electrons, the atomic number of the specimen and the density specimen. The
energy exchange between the electron beam and the sample results in the reflection of
high-energy electrons by elastic scattering, emission of secondary electrons by
inelastic scattering and the emission of electromagnetic radiation, each of which can
be detected by specialized detectors. The beam current absorbed by the specimen can
also be detected and used to create images of the distribution of specimen current.
Electronic amplifiers are used to amplify the signals. The resulting image is therefore
a distribution map of the intensity of the signal being emitted from the scanned area of
the specimen. A camera is used to photograph the image or it may be digitized and
processed on a computer. Essential requirement is that the sample should be
conductive. Surface of non-conductive samples are rendered conductive usually by
coating a thin layer of gold. In the present the SEM measurements were carried out at IUAC, New Delhi using MIRA II LMH from TESCAN with a resolution of 1.5 nm at 30 kV.

2.3.4 Transmission electron microscope:

Transmission electron microscopy (TEM) is a microscopy technique used to obtain structural information from specimens that are thin enough to transmit electrons. TEMs are capable of imaging at a significantly higher resolution than light microscopes, owing to the small de Broglie wavelength of electrons. This enables the instrument's user to examine fine detail—even as small as a single column of atoms,
which is tens of thousands times smaller than the smallest resolvable object in a light microscope. A beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera. Figure 2.11 shows the schematic of TEM. Electrons thermionically emitted from the gun are accelerated to 100 keV or higher (1 MeV in some microscopes) and first projected onto the specimen by means of the condenser lens system [14]. These electrons are scattered at different angles depending on the density of the atom it encounters. An electron can either be (a) undeflected, (b) deflected but loses no energy (elastically deflected), or (c) loses a significant amount of energy and is probably deflected (inelastically scattered). The different scattered angles produce a contrasting image because all angle scattered more than 0.5 degrees are stopped by an objective aperture (figure 2.11) situated below the specimen. The image is projected on a fluorescent screen where phases, fractures and other properties that are 2 to 3 angstroms across, can be seen. To produce a bright-field image, the aperture is inserted so that it allows only the main un-deviated transmitted electron beam to pass. The bright-field image is observed at the detector or viewing screen. If the aperture is positioned to select only one of the beams reflected from a particular hkl plane, the result is the generation of a dark-field image at the viewing screen. A technique called image processing can be used to increase the information obtained from a TEM image, and enhance some features that are close to the noise level. If the image is Fourier-transformed by highly efficient technique called fast Fourier transformation, then it provides information similar to that in the direct diffraction patterns. In the present thesis, TEM model FEI, Tecnai F20 G2 TEM, performed at 200 kV at Korea Institute of Science and Technology (KIST), Korea is used.

2.3.5 Atomic force microscopy (AFM):

Atomic force microscopy (AFM) is one of the most powerful tools for determining the surface topography of specimens at sub-nanometer resolution. It reproduces the image of the sample surface using a sharp tip as a probe which is
commonly made from silicon or silicon nitride which is attached to a flexible cantilever with a specific spring constant. The tip and the surface of the sample interact via Van der Waals forces during scanning. The cantilever detects in the Z-direction due to the interaction. A laser reflecting off the cantilever is tracked by a split photodiode detector [15]. The computer processes the electrical differential signal of the photodiode obtained from each point of the surface and generate a feedback signal for a piezo-scanner to maintain a constant force on the tip. This information is then processed into a topographical image. Figure 2.12 shows the schematic diagram of AFM.

![Schematic diagram of AFM](image)

Figure 2.12: Schematic diagram of AFM.

Three basic operating modes: contact mode, tapping mode and non-contact mode are used for the surface analysis. In tapping mode, the cantilever is oscillated near its resonance frequency with the amplitude ranging typically from 20 to 100 nm. When the tip comes close to the surface, it “taps” the surface and the forces of interaction acting on the tip such as Van der Waals force, dipole-dipole interaction, electrostatic forces, etc. cause the amplitude of this oscillation to decrease. An
electronic servo uses the piezoelectric actuator to control the height of the cantilever above the sample. The servo adjusts the height to maintain a set cantilever oscillation amplitude as the cantilever is scanned over the sample. A tapping AFM image is therefore produced by imaging the force of the intermittent contacts of the tip with the sample surface. In the present work, to study topographic and morphology of the thin films, Atomic Force Microscopy (AFM) measurements have been carried out using Nanoscope III a (Digital Instruments) at IUAC, New Delhi, India.

2.3.6 Magnetic force microscope:

![Diagram of magnetic force microscope](image)

Figure 2.13: Schematic for the mapping of the magnetic domains of the sample surface using MFM.

Magnetic force microscope (MFM) is a variant of atomic force microscopy [16]. A flexible cantilever beam with a sharp magnetic probe on its end is used as a force sensor. In this technique, a magnetic probe is brought close to a sample typically between 10 to 100 nm, the magnetic interaction between the tip and sample can give rise to a change of the cantilever status, such as static deflection or resonant frequency as shown in figure 2.13. As the MFM tip is raster scanned across the sample, this change can be used to form a two dimensional magnetic image. An image contains information about both the topography and the magnetic properties of a surface. Its effect depends upon the distance of the tip from the surface, because the inter-atomic magnetic force persists for greater tip to sample separation than the van der Waals
force. If the tip is close to the surface, in the region where standard noncontact AFM is operated, the image will be predominantly topographic. As the separation between the tip and the sample, the magnetic effect becomes apparent. MFM detects the force or force gradient between the MFM tip and magnetic sample [17]. The magnetic force between the sample and the tip can be written as

\[ F = \mu_0 (m \cdot \nabla) H \]  

(2.3)

where \( m \) is the magnetic moment of the tip, \( H \) is magnetic stray field from the sample surface and \( \mu_0 \) is the magnetic permeability of free space.

2.3.7 Rutherford backscattering spectroscopy:

![Schematic diagram of a typical backscattering spectrometry system](image)

Fig 2.14: Schematic diagram of a typical backscattering spectrometry system [18].

Rutherford backscattering spectroscopy (RBS) is a well-established technique in thin film characterization in which a beam of high energy (2 MeV) helium ions is directed at a sample. The helium ions elastically scattered by nuclei in the sample are detected. The higher the mass of an atom that is hit by a helium ion, the higher the energy of the ion will be after backscattering. This results in mass discrimination. By counting the helium ions as a function of energy, the number of atoms of each
element present can be determined. The basic principle is contained in the kinematics for binary collisions. For an incident particle of mass $M_1$ having energy $E_0$ collides with a target atom of mass $M_2$ at rest. Let $E_1$ be the energy on backscattered and $\theta$ be the scattering angle. Then kinematic factor may be defined as the ratio of the energy of the backscattered and incident particle.

$$k = \frac{E_1}{E_0} = \left( \frac{M_1^2 - M_2^2 \sin^2 \theta}{M_2 + M_1} \right)^{\frac{1}{2}} \left( M_2 + M_1 \right)^2$$ (2.4)

The energy $E_1$ and the scattering angle $\theta$ of the particle $M_1$ are detected. From the conservation of laws of energy and momentum, it is then possible to deduce the mass of the target particles $M_2$. Furthermore, since the probability of scattering in a certain angle is known by the so called Rutherford cross section, it is also possible to estimate the abundance of $M_2$ particles in the sample by counting the yield of scattered particles $M_1$ in a certain solid angle covered by the detector. A typical Rutherford backscattering setup is shown in figure 2.14. In the present experiment, RBS facility with 1.7 MV pelletron accelerator installed in IUAC, New Delhi has been used. The facility is equipped with Alphatross ion source, 1.7 MV 5 SDH-2 pelletron accelerator. Surface barrier detector measures the backscattered ion energy and number.

### 2.3.8 Two-probe resistivity measurement:

The two probe method is one of the standards and most commonly used method for the measurement of resistivity of very high resistivity samples like sheets/films of polymers. The resistivity measurement of such samples is beyond the range of Four Probe Method. In this method, the resistivity $\rho$ can be measured by measuring voltage drop across the sample due to passage of known constant current through the sample as shown in figure 2.15. Current source is used to flow a known constant value of current through the specimen using the two probes (in through probe 1 and out through probe 2). Let the current in the specimen is $I$ (ampere) which is measured by ammeter $A$. The potential difference between the two contacts (probe 1 and probe 2) is $V$ (volt) and is measured by voltmeter $V$. Thus the resistance $V/I$ is known and the resistivity of the specimen is
\[ \rho = \frac{V A}{I l} \]  \hspace{1cm} (2.5)

where \( A \) is the area of cross-section and \( l \) is the length of the specimen between the two probes.

The resistivity measurements, in the present work, were performed using the standard two-probe resistivity measurement using Keithley 2612A Source meter. The temperature of the sample is controlled using the Lakeshore temperature controller (Model 340) and stabilized within \( \pm 50 \) mK. This setup is fully automated and program had been written using Lab-View software.

![Diagram of two probe method](image)

Figure 2.15: Two probe method of measuring resistivity.

2.3.9 Dielectric spectroscopy:

The frequency and temperature dependent dielectric properties of CoIn\(_x\)Fe\(_2\)O\(_4\) (\(x=0, 0.15\)) samples have been carried out with the automated dielectric measurement set up at IUAC, New Delhi. For these measurements, the powder samples were pelletized and silver were coated on both the faces making parallel plate capacitor geometry with CFO as the dielectric medium. The set up consists of LCR meter (Agilent 4285A precision) with frequency range 75 KHz–1MHz. A homemade sample holder in the form of ladder as shown in figure 2.15 is connected to the LCR meter. This was designed to put the sample in the liquid nitrogen container for low
temperature. The temperature can be varied within 80K–400 K. The temperature of the sample is controlled using the Lakeshore temperature controller (Model 340) and stabilized within ± 50 mK. This setup is fully automated and interfaced with PC using Lab-View software.

Figure 2.16: The schematic of Dielectric measurement set up and set up and the sample ladder for mounting the samples.

The value of dielectric constant ($\varepsilon'$) has been calculated using the formula:

$$\varepsilon' = \frac{\varepsilon'_p}{\varepsilon_0/4}$$  \hspace{1cm} (2.6)
where \( \varepsilon_0 = 8.854 \times 10^{-12} \text{ F/m} \), known as permittivity of free space, \( t \) is the thickness of pellets, \( A \) is the area of cross section of the pellet and \( C_p \) is capacitance of the pellet. The imaginary dielectric constant has been calculated from the relation:

\[
\varepsilon'' = \varepsilon' \tan \delta
\]

(2.7)

where \( \tan \delta \) is the loss tangent, proportional to the energy loss from the applied field into the sample (in fact this energy is dissipated into heat) and therefore denoted as the dielectric loss [19]. The ac conductivity is calculated from the data of dielectric constant and loss tangent (\( \tan \delta \)) using the relation;

\[
\sigma_{ac} = \varepsilon' \varepsilon_0 \omega \tan \delta
\]

(2.8)

where \( \omega = 2\pi f \).

2.3.10 Vibrating sample magnetometer:

A vibrating sample magnetometer (VSM) is a versatile and sensitive technique used to measure magnetic properties of material [20]. The principle of this measurement is based on Faraday's law which states that an electromagnetic force is generated in a coil when there is a change in flux linking the coil [21]. When a sample is placed in a homogenous magnetic field, a magnetic moment is induced in the sample which is proportional to the product of susceptibility and the applied magnetic field. If this sample is made to undergo sinusoidal motion, it induces a magnetic flux change. This in turn induces a voltage in the pick-up coils. Figure 2.17 shows the schematic of VSM set up. For the measurement, a magnetic sample attached to the end of a nonmagnetic rod is suspended from a vibrating drive head and placed at the center of the two pole pieces of an electromagnet that generates a homogenous magnetic field. The vibrator generates a sinusoidal signal that is translated by the transducer assembly into a vertical vibration. The sample which is fixed to the sample rod vibrates with a given frequency and amplitude. The oscillating magnetic field of the moving sample induces an electric signal in the coils mounted on the pole faces of the electromagnets, whose magnitude is proportional to the magnetic moment of the sample. The frequency and amplitude of the sinusoidal motion are maintained constant by a capacitor (reference signal generator). By feeding the signals from the
pick-up coils and the reference signal into a demodulator, the magnetic moment of the sample is extracted. VSM model (EV-9, Microsense) with maximum field of 22 kOe at University of Delhi is used for M-H loops in this thesis.

![Figure 2.17: Schematic representation of VSM.](image)

2.3.11 X-ray absorption spectroscopy and x-ray magnetic circular dichroism:

X-ray absorption spectroscopy (XAS) is a widely used technique for determining the local geometric and/or electronic structure of matter. The experiment is usually performed at synchrotron radiation sources, which provide intense and tunable X-ray beams [22]. In XAS measurements the absorption coefficient is measured as a function of incident photon energy. A direct method for measuring this is to measure the incident X-ray intensity ($I_0$) and the intensity of the X-rays
transmitted from the sample ($I$). These are related according to the Beer-Lambert's law [23]

$$I = I_0 e^{-\mu(E)x}$$

(2.9)

where $x$ is the thickness of the sample and $\mu(E)$ is the absorption coefficient. The characteristic features of the x-ray absorption coefficient are the absorption edges: if the photon energy is large enough to excite an atomic core electron into the continuum, a step-like increase is found in the x-ray absorption coefficient. The name of the edge depends upon the core electron which is excited: the principal quantum numbers n=1, 2, and 3, correspond to the K-, L-, and M-edges, respectively. For instance, excitation of a 1s electron occurs at the K-edge, while excitation of a 2s or 2p electron occurs at an L-edge. Since the energies of the edges (or ionization energies) are unique for a specific element, XAS is element specific. In the vicinity of a specific absorption edge the photoelectric absorption coefficient is dominated by the

Figure 2.18: Various regions of XAS data.
absorption processes which start from this particular core level. The absorption
coefficient $\mu$ can be described by Fermi's golden rule.

There are three main regions found on a spectrum generated by XAS data as
shown in figure 2.18.

(i) The "absorption threshold" determined by the transition to the lowest
unoccupied states: a) the states at the Fermi energy in metals giving a "rising
edge" with an invtan shape; b) the bound core excitons in insulators with a
Lorentzian line-shape (they occur in a pre-edge region at energies lower than
the transitions to the lowest unoccupied level).

(ii) The x-ray absorption near-edge structure XANES also NEXAFS (near-edge
X-ray absorption fine structure) which are dominated by core transitions to
quasi bound states for photoelectrons with kinetic energy in the range from 10
to 150 eV above the chemical potential. In this range multi-electron exitations
and many-body final states in strongly correlated systems are relevant.

(iii) In the high kinetic energy range of the photoelectron the scattering cross-
section with neighbor atoms is weak and the absorption spectra are dominated
by EXAFS (extended x-ray absorption fine structure) where the scattering of
the ejected photoelectron off neighboring atoms can be approximated by
single scattering events.

X-ray magnetic circular dichroism (XMCD) is a difference spectrum of two x-
ray absorption spectra (XAS) taken in a magnetic field, left circularly polarized light,
and one with right circularly polarized light. XMCD is sensitive to magnetic
polarization, and therefore enable us to study the magnetic properties of particular
orbitals on each element. For a magnetic material, XMCD signal arises due to the
dependence of the absorption cross-section on the magnetic state. The concepts of
XMCD are illustrated in figure 2.19. Simple sum rules can be used to separate out the
spin and orbital contributions to the magnetism. The first x-ray absorption sum rule
links the total intensity of the $L_3$ and $L_2$ resonances with the $N$ number of empty $d$
states (holes) [24, 25]. The $d$ valence shell can hold up to 10 electrons which are filled
into band states up to the Fermi level and the number of filled states is therefore $10 - N$. For a magnetic material the $d$ shell has a spin moment which is given by the
imbalance of spin-up and spin-down electrons or equivalently (except for the sign) by
the imbalance of spin-up and spin-down holes. In order to measure the difference in
the number of d holes with up and down spin, we need to make the x-ray absorption
process spin dependent. This is done by use of right or left circularly polarized
photons which transfer their angular momentum to the excited photoelectron.

Figure 2.19: Schematic showing the XMCD concept [26].

The photoelectron carries the transferred angular momentum as a spin or an
angular momentum, or both [27]. If the photoelectron originates from a spin-orbit
split level e.g. the p_{3/2} (L_{3}-edge) and p_{1/2} (L_{2}-edge), the angular momentum of the
photon can be transferred in part to the spin through the spin-orbit coupling. Right
circular photons (RCP) transfer the opposite momentum to the electron as left circular
photons (LCP), and hence photoelectrons with opposite spins are created in the two
cases. The p_{3/2} (L_{3}) and p_{1/2} (L_{2}) levels have opposite spin-orbit coupling, therefore,
the spin polarization will be opposite at the two edges. In the absorption process, spin-
up and spin-down are defined relative to the photon helicity. This is represented in the
figure 2.18.
In the present study, XAS and XMCD experiments were performed at dragon beamline (BL11A1) at National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan. The measurements were performed in an ultrahigh-vacuum (UHV \( \approx 10^{-10} \text{ mbar} \)) chamber. Signals were then recorded in the total-electron-yield (TEY) mode on measuring the sample drain current and normalized to the incoming flux \( I_0 \) as measured on an Au-mesh at the entrance of the experimental chamber.
References:


Chapter 3

Structural, Magnetic and Electrical Properties of CoIn$_x$Fe$_{2-x}$O$_4$ (x=0, 0.15) Nanoparticles

In this chapter, synthesis and characterization of CoIn$_x$Fe$_{2-x}$O$_4$ (x=0, 0.15) nanoparticles is reported. These nanoparticles were prepared by sol-gel citrate route and various experimental techniques were used to investigate the structural, magnetic properties at room temperature, resistivity as a function of temperature and ac conductivity, dielectric as a function of frequency and temperature.
3.1 Introduction:

There are numerous reports on the pristine and chemically doped CFO system, ranging from single crystals [1-3] to thin films [4-9] and nanoparticles [10-18]. The physical properties of these materials are influenced by many factors such as processing temperature and history of heat treatment, compositions, cation distributions, microstructures such as grain size, porosity, presence of defects etc [19-22]. A clean separation of these sets of parameter is not possible because the processing temperature or history of heat treatment affect both the chemical and microstructural aspects of ferrites. Substitution of non-magnetic or magnetic metals for Fe in CFO has been proposed in order to tailor the magnetic, electrical and magnetomechanical properties of such materials. This is considered to be due to the differences in cation site occupancy preferences of the elements within the spinel crystal structure; Mn$^{3+}$ and Cr$^{3+}$ prefer the octahedral (B) sites, whereas Ga$^{3+}$ and Zn$^{2+}$ prefers the tetrahedral (A) sites [19]. The enhancement in electrical properties CFO with the substitution of Zn was reported by Reddy et. al. [23] and Beyoumi et. al. [24]. Kriebel et. al. [25] and Paulsen et. al. [26] reported that magnetic and magnetomechanical properties can be tailored by varying the concentration of Mn. Song et. al. [27] reported on the variation of the Curie temperature $T_C$ and hysteresis properties with the variation of gallium content in CFO. Sometimes, limitations on the desirable properties may be more easily overcome by control of microstructure than by choice of chemistry. Gyergyek et. al. [28] studied the influence of synthesis method on structural and magnetic properties of CFO nanoparticle having uniform particle size around 8 nm, synthesized through three different methods: simple co-precipitation from aqueous solutions and a co-precipitation in an environment of microemulsions which are low temperature methods (50°C) and a thermal decomposition of organo- metallic complexes at elevated temperature of 290°C. Wang et. al. [29] investigated the effects of heat treatment on two samples one slowly cooled and other quenched after annealing at 1000°C and exhibited very different magnetic behaviors. The quenched sample had a much higher saturation magnetization with a relatively low coercivity. Finite size effects on the electrical properties of sol–gel synthesized CFO powders have been studied by George et. al. [10] and found higher permittivity and conductivity for smaller grains.
In this chapter, pure and 15% Indium doped CFO were prepared by sol-gel citrate route. Structural, magnetic and electrical properties were investigated.

3.2 Experimental details:

The stoichiometric amount of nitrates of Fe, Co, In and citric acid were dissolved into deionized water to form mixed solution and heated at 80°C under constant stirring on the magnetic stirrer to allow evaporation until it is converted into gel, containing all cations homogeneously mixed together at atomic level. These gels were heated at 100°C for 24 h in an oven to form loose fluffy powder. The powder was grinded for half an hour and sintered at 600°C for 6 hrs and again grinded for half an hour. To confirm the formation of phase, XRD and Raman spectroscopy were carried out. SEM equipped with EDS was employed to examine the microstructural features and chemical composition of the samples. Magnetic hysteresis loops were measured at room temperature using a VSM with maximum field of 22 kOe. The DC electrical resistivities were measured by two probe method in the temperature range 250K–400K. Dielectric properties were studied as a function of frequency and temperature in the range 75KHz–1MHz and 80K–400 K, respectively. For these measurements, the samples were pelletized and silver was coated on both the faces making parallel plate capacitor geometry with ferrite material as the dielectric medium.

3.3 Results and discussions:

3.3.1 Structural properties:

The structural studies of undoped and 15% In doped CFO were performed by XRD and the results are shown in figure 3.1. The XRD patterns reveal that all the peaks correspond to the characteristic peaks of cubic spinel lattice of CoFe$_2$O$_4$ (JCPDS File No. 22 – 1086) indicating that the samples have a single – phase spinel structure and no unreacted constituents or impurity phases were present in the samples. The average grain size of both the samples was determined from XRD peak broadening using Scherrer’s formula [31]

\[
d = \frac{\alpha \lambda}{\beta \cos \theta}
\]  

(3.1)
where $d$ is the average crystallite size, $\beta$ is the full width at half maximum (FWHM) of the diffraction line of most intense peak measured in radians, $\lambda$ is the X-ray wavelength of the Cu $K_\alpha = 1.54$ Å, and $\theta$ is the Bragg's angle. The value of X-ray density was determined according to the relation [32]

$$D_x = \frac{8M}{Na^3}$$  \hspace{1cm} (3.2)

where $N$ is the Avogadro's number and $M$ is the molecular weight of the sample. The apparent density ($D_a$) was determined from mass and the bulk volume of the sample.

![XRD pattern](image)

**Figure 3.1:** XRD pattern of CoIn$_x$Fe$_{2-x}$O$_4$ ($x=0, 0.15$) with the inset showing broadening and shifting of (311) peak.

The percentage of porosity ($P$) of the samples was calculated from $D_x$ and $D_m$ values using the expression

$$P = \left(1 - \frac{D_m}{D_x}\right) \times 100$$  \hspace{1cm} (3.3)
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Assuming all the particles to be spherical, the specific surface area was calculated from the relation [10]

\[ S = \frac{6000}{d\rho} \]  

(3.4)

where \( d \) is the diameter of the crystallite in nm and \( \rho \) is the density of the particle. The calculated X-ray density, apparent density, porosity and surface specific area are given in table 3.1. The average grain size decreases whereas the lattice parameter expands which may be due to larger ionic radii \( \text{In}^{3+} \) (0.78Å) replaces the smaller \( \text{Fe}^{3+} \) (0.69Å) ions.

Table 3.1: Structural parameters of the In doped CFO nanoparticles.

<table>
<thead>
<tr>
<th>Sample CoInₓFe₂₋ₓO₄</th>
<th>Grain Size (nm)</th>
<th>Lattice parameter (Å)</th>
<th>Theoretical Density ( D_x ) (gm/cm³)</th>
<th>Apparent Density ( D_m ) (gm/cm³)</th>
<th>Porosity (%)</th>
<th>Specific Surface Area (m²/gm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x=0.0</td>
<td>44.43</td>
<td>8.37</td>
<td>5.32</td>
<td>3.02</td>
<td>43</td>
<td>44.65</td>
</tr>
<tr>
<td>x=0.15</td>
<td>22.37</td>
<td>8.39</td>
<td>5.47</td>
<td>2.84</td>
<td>47</td>
<td>99.44</td>
</tr>
</tbody>
</table>

Table 3.2: Composition of the In doped CFO nanoparticles measured from EDS.

<table>
<thead>
<tr>
<th>Sample CoInₓFe₂₋ₓO₄</th>
<th>Composition measured from EDS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co (at %)</td>
</tr>
<tr>
<td>x=0.0</td>
<td>15.10</td>
</tr>
<tr>
<td>x=0.15</td>
<td>14.44</td>
</tr>
</tbody>
</table>

The SEM images and EDS spectra of the samples are shown in figure 3.2. The SEM images clearly show that the samples are in the nano-regime and the EDS spectra confirmed the presence of all constituent elements with nearly expected elemental composition as given in table 3.2.
Figure 3.2: SEM micrograph and EDS spectra of Coln_xFe_{2-x}O_4 (a & b) x=0 and (c & d) x=0.15.

For confirmation of phase purity of pure and doped nanoparticles, Raman spectra were also recorded at room temperature as presented in figure 3.3. Ferrites crystallizes in cubic spinel structures belonging to the space group Fd3m (O^7_h No. 227). Group theory predicts following phonon modes for the spinel structure

$$A_{1g}(R) + E_g(R) + T_{1g} + 3T_{2g}(R) + 2A_{2u} + 2E_u + 4T_{1u} (IR) + 2T_{2u}$$  (3.5)

Out of these phonon modes five are Raman active ($A_{1g} + E_g + 3T_{2g}$) and four infrared active modes ($4T_{1u}$). All the five Raman active modes were observed at ambient conditions. The modes above 600 cm^{-1} correspond to the modes of tetrahedral group
(A – sites) that reflects the local lattice effect in the tetrahedral sublattice and those below 600 cm\(^{-1}\) represent the modes of octahedral group (B – sites) and reflects the local lattice effect of the octahedral sublattice. This is consistent with the previously reported studies [33, 34] therefore it is confirmed that the samples are single phase cubic spinel structure. The modes exhibit a red shift with broadening of FWHMs in the doped sample which may be due to the strain developed in the lattice and the decrease of grain size [34, 35]. The doping of larger ionic radius In\(^{3+}\) ions (0.78Å) forces the lattice to expand which develop a strain in the lattice. The development of strain in the lattice is also seen in the XRD spectrum shown in figure 3.1 as a shift of the diffraction peaks and expansion of lattice constant given in Table 3.1. Chandramohan et. al. [34] reported that red shift with broadening of peak are due to the decrease of grain size. In nano - crystals, unlike the crystalline materials, due to lack of long range order, not only the phonons with q=0 but also those with q > 0 take part in the scattering process leading to broadening and shift of peak position in the Raman Spectra.

![Figure 3.3: Raman Spectra of CoIn\(_2\)Fe\(_{2+x}\)O\(_4\) (x=0, 0.15).](image-url)
3.3.2 Magnetic Properties:

Magnetization measurements were performed at the room temperature and the results are shown in figure 3.4. The value of coercivity ($H_c$), remnant magnetization ($M_r$), saturation magnetization ($M_s$) are listed in Table 3.3. In ferrites, magnetic properties are strongly influenced by the site preference of cations in the spinel lattice [20]. There are three kinds of exchange interactions between the magnetic ions lying on two different sublattices of ferrite i.e. AA interaction, BB interaction and AB interactions. AB interaction predominates over AA or BB interactions [36]. The net magnetic moment is the difference in moments of B and A sublattices i.e. $M = M_B - M_A$. Magnetic properties of ferrite depend not only on the chemical composition which determines the intrinsic properties, but also on various extrinsic factors such as grain sizes, porosity and density [36]. In the literature [21, 37] it is reported that In$^{3+}$ ions prefer to occupy A sites at lower concentrations (upto $x = 0.3$). If In$^{3+}$ ions occupy A – sites and replace Fe$^{3+}$ ions, the A sublattice magnetization will decrease and the net magnetization will therefore increase. In the present case the magnetization decreases and coercivity increases in the In$^{3+}$ doped sample which are contrary to the previous observation of Indium doping as reported by Shirsath et. al. [21] and Lakshman et. al. [37]. Therefore, the observed result may be attributed to the decrease of grain size and increase of porosity. The coercivity of fine particles has striking properties on their size. As the grain size decreases, the coercivity increases, goes through a maximum then decreases and become zero for a very small size known as superparamagnetism. The change in coercivity is due to the change of the multidomain nature to single domain. In the multidomain region the size dependence of coercivity is expressed as [38]

$$H_c = a + \frac{b}{D} \quad (3.6)$$

where $a$ and $b$ are constants and $D$ is the diameter of the particle. A porous sample also implies lesser number of magnetic moments in the specified volume which results in the decrease of magnetization. The saturation magnetization is related to $H_c$ through Brown’s relation [20]

$$H_c = \frac{2K_s}{\mu_0 M_s} \quad (3.7)$$
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According to this relation $H_e$ is inversely proportional to $M_s$ which is consistent with our experimental results. The increase in coercivity in the doped sample shows that hard ferrite nature retains with In substitution.

Table 3.3: Electric and Magnetic Properties of the synthesize nanoparticles.

<table>
<thead>
<tr>
<th>Sample CoIn$<em>x$Fe$</em>{2-x}$O$_4$</th>
<th>Electric Properties</th>
<th>Magnetic Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Resistance ($\Omega$)</td>
<td>Activation energy (eV)</td>
</tr>
<tr>
<td>$x=0.0$</td>
<td>$8 \times 10^6$</td>
<td>0.19</td>
</tr>
<tr>
<td>$x=0.15$</td>
<td>$3 \times 10^7$</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Figure 3.4: Hysteresis loops of CoIn$_x$Fe$_{2-x}$O$_4$ ($x=0.0, 0.15$) at room temperature.

3.3.3 Electrical Properties:

Temperature variation of DC electrical resistivity ($\rho$) has been studied and figure 3.5 shows the results measured in the temperature range of 250K – 400K. It is observed that the resistivity decreases with increasing temperature which reflects the semiconductor behavior. The decrease in resistivity with temperature is due to the
increase in the drift mobility of the charge carriers which are thermally activated upon increasing the temperature. In ferrites, the electrons are localized with little probability of overlapping of wavefunctions of ions located at adjacent sites. However, in the presence of lattice vibrations, the ions come close enough and the transfer of electrons from one ion to another occurs with high probability [39]. Hence the mobility is enhanced with temperature. The activation energies are obtained by fitting the DC resistivity data with the Arrhenius relation

\[ \rho = \rho_0 \exp \left( \frac{E_a}{kT} \right) \]  

(3.8)

where \( E_a \) is the activation energy and \( k \) is the Boltzmann constant. The activation energy of the samples is given in Table 3.3. It is also observed that DC resistivity increases in the \( \text{In}^{3+} \) ions doped sample which may be due to the decrease of grain sizes. Smaller grains imply a larger number of insulating grain boundaries which hindered the motion of charge carriers. Smaller grains also reduce the grain to grain surface contact area and therefore reduce the motion of charge carriers hence the resistivity increases.

![Graph showing the variation of log \( \rho \) with temperature for \( \text{CoIn}_x\text{Fe}_{2-x}\text{O}_4 \) (\( x = 0, 0.15 \)).](image)

Figure 3.5: The variation of log \( \rho \) with temperature of \( \text{CoIn}_x\text{Fe}_{2-x}\text{O}_4 \) (\( x = 0, 0.15 \)).
Figure 3.6: The variation of $\sigma_{ac}$ with frequency of CoIn$_{2}$Fe$_{2x}$O$_{4}$ (x = 0, 0.15) at room temperature.

The electric conductivity of a dielectric material is a summation of two terms [40]

$$\sigma = \sigma_0(T) + \sigma(\omega, T)$$ (3.9)

The first term $\sigma_0(T)$ is frequency independent or dc conductivity which is related to the drifting of charge carriers and follows an Arrhenius relation. The second term $\sigma(\omega, T)$ is frequency dependent function and is related to the dielectric relaxation caused by the localized electric charge carriers which obeys the empirical power law [41]

$$\sigma(\omega) = A\omega^n$$ (3.10)

where the constants A and n are both temperature and composition dependent parameters; n is dimensionless whereas A has units of conductivity and $\omega$ is angular frequency. Figure 3.6 shows the variation of ac conductivity with frequency at room temperature. Initially, ac conductivity increases with the increase of frequency but at higher frequency conductivity tend to decrease with further increase of frequency.
Figure 3.7: The variation of $\sigma_\infty$ with temperature at selected frequencies of CoIn$_x$Fe$_{2-x}$O$_4$ (a) $x=0$ and (b) $x=0.15$.

The conduction mechanism in ferrites is explained on the basis of hopping of electron between Fe$^{2+}$ and Fe$^{3+}$ ions at octahedral sites. As the frequency of applied field increases the hopping frequency of electron enhances which cause an increase in the mobility of charge carriers. Thus we observe a gradual increase in conductivity with frequency. But at higher frequencies, the hopping of electron cannot follow the applied field frequency and it lags behind it which results to the decrease of
conductivity. The increase in conductivity does not mean the increase in charge concentration but increase in mobility of charge carriers. The relaxation frequency in ac conductivity is observed to decrease with the doping of In\(^{3+}\) ions. Since the doped sample has smaller grain size and higher grain boundaries present in them, the conductive grain volume which become more active at higher frequencies is lesser than the undoped sample. Thus conductivity begins to decrease at lower frequency.

Variations of ac conductivity with temperature at selected frequencies for the pure and doped sample are shown in figure 3.7 (a) and (b) respectively. The ac conductivity increases with the increase of temperature for all frequencies. However such an increase is more rapid at higher frequencies. This increase in the conductivity with the increase in temperature is due to the increase in drift mobility of the charge carrier thereby enhancing the charge hopping.

![Graph showing the variation of s' with frequency](image)

**Figure 3.8:** The variation of s' with frequency of \( \text{CoIn}_x\text{Fe}_{2-x}\text{O}_4 \) \((x = 0, 0.15)\) at room temperature.

The dielectric properties were investigated as a function of frequency and temperature. The dielectric constant is represented by
\[ \varepsilon = \varepsilon' - j\varepsilon'' \]  
(3.11)

where \( \varepsilon' \) is the real part which represents the stored energy and \( \varepsilon'' \) is the imaginary part which represents the dissipated energy. The dielectric properties of ferrite materials are influenced by many factors like method of preparation, structural homogeneity, cation distribution, grain size, density, porosity, history of sintering etc [20, 21]. Figure 3.8 illustrates the frequency dependence of real part of dielectric constant at room temperature. The dielectric constant decreases with increase in frequency which is common behavior in ferrites. The observed dispersion is qualitatively due to interfacial polarization in accordance with the Maxwell – Wagner model [42]. In this model, the dielectric materials are assumed to be composed of conducting grains separated by poorly conducting grain boundaries. The mechanism of polarization in polycrystalline ferrite is reported to be the hopping of electrons between ions of the same element in different oxidation states at B – site [43, 44]. When a field is applied the electron flow in the direction of the field within the grain through hopping and pile up at the grain boundaries to produce polarization. If the frequency of the field increases, the electrons cannot keep up with the field and the alteration of their direction lags behind that of the field. As a result, the probability of electrons reaching the grain boundaries decreases. This decreases the polarization and hence the dielectric constant. Iwauchi [45] pointed out that there is a strong correlation exists between the conduction mechanism and the dielectric behavior of the ferrites, i.e., the mechanism of polarization in ferrites is a similar process to that of conduction. Jonker [44] studied the electrical conduction of a series of ferrites Co\(_{1-x}\)Fe\(_{2+x}\)O\(_4\) and observed that the conduction in ferrites is the result of electron hopping between Fe\(^{3+}\) – Fe\(^{2+}\) ions and hole hopping between Co\(^{2+}\) – Co\(^{3+}\) ions. As the field frequency increases the electronic exchange between Fe\(^{3+}\) – Fe\(^{2+}\) and Co\(^{2+}\) – Co\(^{3+}\) cannot follow the rapid field variation and it lags more and more behind the field therefore the polarization decreases. The dielectric constant in the present study is of the order of 10\(^2\) which is an order of magnitude higher as compared to that reported by Sivakumar et. al. [11] and George et. al. [10] at the same temperature and frequency. Introduction of small amount of In\(^{3+}\) ions (x = 0.15) results in the increases of dielectric constant which can be attributed to the decrease in grain size. Decrease in grain size results in larger number of both grains and grain boundaries. These grain
boundaries act as a scattering center. Also, smaller grains provide large surface polarization resulting from large surface area of individual grains. As discuss above that In$^{3+}$ ion replace Fe$^{3+}$ ion in the A – sites, it is reasonable to assume that the number of Fe$^{3+}$ - Fe$^{2+}$ and Co$^{2+}$ - Co$^{3+}$ ions retains in the B – sites. Therefore, microstructures play a dominant role in determining the dielectric property.

The dielectric loss ($tan \delta$) in ferrites is a measure of lag in the polarization with respect to the alternating field. Variations of dielectric loss as a function of frequency are shown in figure 3.9. The behavior of dielectric loss is normally reflected in the resistivity measurement; with the high-resistivity materials exhibit low dielectric losses and vice – versa.

![Graph](image)

Figure 3.9: The variation of $tan \delta$ with frequency of CoIn$_x$Fe$_{2-x}$O$_4$ ($x = 0, 0.15$) at room temperature.

The temperature dependence of the dielectric constant at selected frequencies is shown in figure 3.10. At low temperature both the dielectric constant and dielectric loss are independent of temperature whereas at higher temperature there is an increase with temperature for all frequencies. This is due to the fact that at higher temperatures extra thermal energy supplied by the temperature boost the mobility of charge carrier
hence their rate of hopping is enhanced while the thermal energy supplied at lower temperature are not enough for the increase of mobility of charge carriers. The dielectric polarization therefore increases at higher temperature causing an increase in dielectric constant and dielectric loss with temperature.

It is observed that the temperature dependence of the dielectric constant is different at various frequencies, the increase being more rapid at lower frequencies than at higher frequencies. Dielectric constant is a result of the contribution of four

Figure 3.10: The variation of $\varepsilon'$ with temperature at selected frequencies of $\text{CoIn}_{x}\text{Fe}_{2-x}\text{O}_{4}$ (a) $x=0$ and (b) $x=0.15$. 
Figure 3.11: The variation of $\tan \delta$ with temperature at selected frequencies of CoIn$_{x}$Fe$_{3-x}$O$_{4}$
(a) $x=0$ and (b) $x=0.15$.

types of polarizations namely interfacial, dipolar, ionic and electronic [46]. The rapid increase in dielectric constant at lower frequencies is due to interfacial and dipolar polarization. These types of polarizations show strong dependence on frequency and temperature. At high frequencies contribution to dielectric constant is due to electronic and ionic polarization only, which are independent of temperature. Hence, the effect of temperature on high frequency dielectric constants is of little significant resulting in low dispersion of dielectric constant. This explains the observed
temperature dependence of dielectric constant at various frequencies. The temperature dependence of dielectric loss at selected frequencies is illustrated in figure 11. It is observed that the behavior is similar to that of the dielectric constant which can also be explained in a similar way as in the case of dielectric constant.

3.4 Conclusion:

Nanoparticles of CFO and 15% In CFO were prepared by citrate – gel method. The substitution of In ions at Fe sites results in significant changes in the physical properties of cobalt ferrite. It is observed that the average grain size decreases whereas lattice constant, porosity and specific surface area increase in the In doped sample. Magnetization measurements show that saturation magnetization decreases whereas there is an increase in the coercivity which is attributed to the decrease of grain size and increase of porosity. The results of dc conductivity, dielectric spectroscopy study have shown that there is improvement in the electrical properties. The high resistivity and low dielectric loss led the material suitable for power application at higher frequencies. The present investigation clearly point out that the physical properties of cobalt ferrite depends on the extrinsic factors like grain size, microstructure etc.
References:


Chapter 4

Growth and Study of Structural, Magnetic and Electrical Properties of CoFe$_2$O$_4$ Thin Films

This chapter presents the deposition of CFO thin films by PLD and rf sputtering techniques on quartz and Si substrates and their characterizations. This work was carried out to investigate the effect of growth conditions on the films especially on the structural, magnetic and electrical properties.
4.1 Introduction:

Thin films of CFO have attracted much attention in recent years as one of the potential candidates for high density magnetic and magneto-optical recording media because of their unique physical properties such as high Curie temperature, large magnetic anisotropy, moderate magnetization, excellent chemical stability and large Kerr and Faraday rotations [1-4]. However, an important issue is in making CFO thin films to meet the requirements of high coercivity, perpendicular anisotropy and small grain size for high density magnetic recording media and to fabricate films using a simple technology with low temperature heat treatment and low vacuum [5-7]. Many groups have investigated CFO films fabricated by various sample preparation methods and conditions, to achieve the properties of interest. Kitamoto et. al. [7] prepared CFO films on the Corning 7059 glass substrate at 90°C using the spin-spray ferrite-plating method. The films grown by this method showed no texture but exhibited perpendicular anisotropy with the out-of-plane coercivity of over 2 kOe. Ding et. al. [8] obtained a high coercivity value of 4.9 kOe without magnetic anisotropy or preferred orientation when grown on Si wafer using magnetron sputtering after post-annealing at 700°C. Gu and Hua [9] achieved nanocrystalline textured CFO films by rf sputtering on quartz substrate with directions along (111), (220) and (311), with a maximum coercivity of only 2.8 kOe without anisotropy after annealing at 400°C. However, CFO films epitaxially grown on single crystal substrate such as MgO, SrTiO₃, Al₂O₃ by PLD are able to achieve magnetic anisotropy [10-15]. But the significance is to develop CFO films with perpendicular anisotropy and high coercivity at low deposition temperature and on cheaper substrates than MgO such as amorphous glass or single crystal quartz and Si substrates, compatible with the modern microelectronics technique [5]. In this work, thin films of CFO have been deposited by using PLD and rf sputtering techniques on quartz and Si substrates. These films were characterized to understand structural, magnetic and electrical properties.

4.2 Experimental details:

The thin films of CFO were grown on quartz, SiO₂/Si (100) substrates using the target, prepared by citrate-gel method by both PLD and rf sputtering techniques.
The preparation of the target and the mechanism of deposition techniques were discussed in chapter 2. In case of PLD, the base pressure of the chamber before deposition was pumped down to $6\times10^{-6}$ Torr and $1\times10^{-6}$ Torr for rf sputtering. Table 4.1 and 4.2 summarizes the deposition conditions of the CFO films grown on quartz and SiO$_2$/Si (100) substrates by PLD and rf sputtering techniques respectively. In both the techniques, the target-substrate distance was kept at 5 cm. After deposition, the films were cooled to the room temperature under same pressure. The thicknesses of these films were measured by stylus profilometer. XRD, Raman Spectroscopy, AFM and RBS were used for structural characterization whereas VSM and two probe resistivity measurement were used for magnetization and dc resistivity measurement.

**Table 4.1: Deposition conditions of CFO films grown by PLD.**

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Substrate</th>
<th>Laser Energy (mJ)</th>
<th>Repetition rate (Hz)</th>
<th>Growth Temp. $T_s$ (°C)</th>
<th>O$_2$ Pressure (mT)</th>
<th>Film Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFO1</td>
<td>Quartz</td>
<td>200</td>
<td>10</td>
<td>500</td>
<td>20</td>
<td>41</td>
</tr>
<tr>
<td>CFO2</td>
<td>Si</td>
<td>164</td>
<td>10</td>
<td>500</td>
<td>20</td>
<td>41</td>
</tr>
<tr>
<td>CFO3</td>
<td>Si</td>
<td>188</td>
<td>10</td>
<td>500</td>
<td>20</td>
<td>186</td>
</tr>
</tbody>
</table>

**Table 4.2: Deposition conditions of CFO films grown by rf sputtering.**

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Substrate</th>
<th>Rf power (mW)</th>
<th>Growth Temp. $T_s$ (°C)</th>
<th>Ar Pressure (mT)</th>
<th>Post-annealed Temp. (°C)</th>
<th>O$_2$ pressure (mT)</th>
<th>Film Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFO4</td>
<td>Quartz</td>
<td>150</td>
<td>500</td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>60</td>
</tr>
<tr>
<td>CFO5</td>
<td>Quartz</td>
<td>150</td>
<td>500</td>
<td>20</td>
<td>700</td>
<td>20</td>
<td>60</td>
</tr>
<tr>
<td>CFO6</td>
<td>Si</td>
<td>150</td>
<td>500</td>
<td>20</td>
<td>700</td>
<td>20</td>
<td>60</td>
</tr>
</tbody>
</table>
4.3 Results and discussions:

4.3.1 Structural property:

Figure 4.1 (a): XRD of CFO thin films deposited by PLD technique.

X-ray diffraction measurements have been carried out for the structural analysis. Figure 4.1 shows the XRD patterns of CFO thin films deposited by PLD and rf sputtering techniques. From the analysis, it is observed that the diffraction peaks of all the samples except CFO4, correspond to polycrystalline single phase cubic spinel structure of CoFe$_2$O$_4$ (JCPDS File No. 22 – 1086). The film CFO4 showed the amorphous nature. However, it is clearly seen from the figure that all the peaks corresponding to CoFe$_2$O$_4$ are not observed in CFO1, CFO2, CFO5, CFO6 and the peak intensities are also quite different. The intensity of (222) is enhanced whereas the (311) peak is greatly reduced otherwise; it is the most intense peak of the bulk sample. In CFO3 the intensity of (400) peak is enhanced, the intensity ratio (400) / (311) is 71% which is much larger than corresponding value of 20% for the polycrystalline target. Hence, the films CFO1, CFO2, CFO5, CFO6 are partially
textured along (111) direction and CFO3 along (100) direction. Texture evolution of polycrystalline films is mainly due to minimization of total system energy by changing the surface energy of oriented crystal planes and interfacial energy between film and substrate or by changing the elastic strain energy density, which is related to different textured orientation. Using single crystal substrates with small lattice mismatch such as Al₂O₃, MgO with CFO, the interfacial energy has a dominant contribution to minimize the total anisotropy energy. However, when using amorphous or single crystal SiO₂, whose planes show no corresponding lattice matching with any planes of CFO, the interfacial energy has negligible contribution to the total anisotropy energy and then can be neglected [15]. The surface energies ($\gamma$) for different planes of CFO are: $\gamma_{(111)}$ (208 ergs/cm²) < $\gamma_{(100)}$ (1486 ergs/cm²) < $\gamma_{(110)}$ (1916 ergs/cm²) < $\gamma_{(311)}$ (2344 ergs/cm²) [16]. Thus, CFO films intend to be (111) preferred orientation since it is more energetically favorable than other orientations such as (100), (110) or (311). Another factor, which influences the development of the
texture in the thin film, is the packing density of oxygen ions. Since in spinel ferrites, the oxygen packing density is maximum along (111) plane, this also favors the growth along (111) direction [17].

Microstructures and the quality of thin films are strongly influenced by growth conditions. Microstructural characteristics of importance include surface morphology, shapes and sizes of grains and their distributions [18]. Surface morphology of the thin films is characterized by the AFM and the results are shown in figures 4.2. The best known parameter characterizing the morphology of a surface is the root-mean-square (rms) roughness, which expresses the variation of the height function over a two-dimensional substrate with linear size. However, the rms is scan size dependent, thus need to be compared between equal scan sizes. The value of rms roughness of the films was evaluated for $2\times2 \, \mu m^2$ by Nanoscope Software. The morphological images of CFO1, CFO5 and CFO6 films exhibit rough surface with rms surface roughness of 5.42 nm, 12.41 nm and 9.37 nm respectively. The surfaces appear to consist of small particles among which some bigger particles are distributed unevenly forming pillars like pattern. This feature is mainly attributed to the island growth mode as discussed in chapter 1 [19]. However, the presence of larger particles in CFO5 and CFO6 may not be due to island growth mode but to the abnormal grain growth during post-deposition annealing [20]. The size distribution of the pillars calculated from the AFM micrograph is shown in figure 4.3. For CFO2, the surface has relatively uniform microstructure with roughness of 1.1 nm. However, a ditch structure is noticed. Ghosh et. al. observed the similar structure at SHI irradiated Li-Mg ferrite thin films [21]. The grains appear to be uniform size (below 20nm) and are agglomerated. A drastic reduction in surface roughness to 0.64 nm and 0.65 nm is observed for CFO3 and CFO4 respectively, indicating a uniform and highly flattened surface. Such a flattened surface could be indicative of a layer by layer growth mechanism as discussed earlier in chapter 1.
Figure 4.2 (a): AFM 2D and 3D images of CFO films grown by PLD.
Figure 4.2 (b): AFM 2D and 3D images of CFO films grown by rf sputtering.
Figure 4.3: The size distribution of the pillars (Bigger particles) calculated from the AFM micrograph.

RBS was performed for the CFO1, CFO2 and CFO3 films and were fitted using RUMP simulation code. Figure 4.4 shows the experimental and simulated RBS spectra. There is no diffusion at the interface. The thickness and the composition of films were estimated from the fitting of experimental spectra and the result are summarized in table 4.3. There is variation in the composition of the film but the ratio Co:Fe is approximately equal. This variation may be due to the slight variation of O₂ pressure during deposition.
Figure 4.4: Experimental and simulated RBS spectra.

Table 4.3: Elemental composition of films estimated from the fitting of experimental spectra.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elements</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cobalt</td>
<td>Iron</td>
<td>Oxygen</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Atomic % calculated from</td>
<td>Atomic % calculated from</td>
<td>Atomic % calculated from</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>formula</td>
<td>RBS fitting</td>
<td>formula</td>
<td>RBS fitting</td>
<td>formula</td>
</tr>
<tr>
<td>CFO1</td>
<td>14.62</td>
<td>17</td>
<td>28.54</td>
<td>32</td>
<td>57.28</td>
</tr>
<tr>
<td>CFO2</td>
<td>14.62</td>
<td>14.1</td>
<td>28.54</td>
<td>28.5</td>
<td>57.28</td>
</tr>
<tr>
<td>CFO3</td>
<td>14.62</td>
<td>18</td>
<td>28.54</td>
<td>32</td>
<td>57.28</td>
</tr>
</tbody>
</table>
4.3.2 Magnetic property:

Figure 4.5: M-H loops of CFO thin films grown by PLD and rf sputtering techniques

The magnetic hysteresis loops were measured by VSM at room temperature both in-plane and out-of-plane configurations in magnetic fields up to 22 kOe. The in-plane and out-of-plane configurations represent the application of the magnetic fields parallel and perpendicular to the film planes. All the hysteresis loops were obtained after subtracting the diamagnetic and paramagnetic contribution from the substrates.
Figure 4.5 shows the hysteresis loops of all samples. All samples showed clear hysteresis loops for both in-plane and out-of-plane. However, the value of remnant magnetization ($M_r$) and coercivity ($H_c$) are different along these two directions suggesting that the films possess magnetic anisotropy. Table 4.4 lists the remanant magnetization ($M_r$) and coercivity ($H_c$) in both orientations, and differences in remnant magnetization ($\Delta M_r$) and coercivity ($\Delta H_c$) between the in-plane and out-of-plane hysteresis loops from figure 4.5. These values are comparable with values reported by Cho et al. and Wang et al. [14, 22]. The remanant magnetization in the out-of-plane direction is larger than that in the in-plane direction for most films which suggest perpendicular magnetic anisotropy (PMA) in the films [23]. However, the smaller value of $\Delta M_r$ in the samples CFO1, CFO5 and CFO6 indicate decrease in perpendicular magnetic anisotropy in these samples. On the other hand, the in-plane coercivity is larger than out-of-plane coercivity in these samples. Furthermore, the small value of $\Delta M_r$, large in-plane ($H_c$) and well saturated in-plane loops of CFO5 suggest that the film exhibits in-plane magnetic anisotropy.

Magnetic anisotropy results from several sources. It can be due to crystal structure i.e. crystallographic texture, the internal stress or strain as well as from the particular shape or arrangement of particles and any one of them may become predominant under special circumstances [23, 24]. In reduced symmetry system like thin films, besides intrinsic crystal anisotropy, extrinsic anisotropy like shape, stress anisotropies are drastically enhanced; competes with each other and may lead to reorientation or modification of anisotropy depending on the predominant source of anisotropy [12]. The origins of these anisotropies in thin films were discussed in chapter 1. In general, the magnetization in thin films lies in the plane of the film, because a huge demagnetizing field would act normal to the plane of the film if $M_r$ were turned in that direction. However, under special conditions of deposition and choice of the substrates, the magnetization is forced to align perpendicular to the film plane due to the dominance of stress anisotropy. In the present case, perpendicular magnetic anisotropy is observed for all samples except CFO5 irrespective of the direction of texture or substrates taken. This can be explained on the basis of dominant contribution of stress anisotropy resulted due to the difference in the thermal expansion coefficient of the substrate (quartz and Si) and the film (CFO). Due
to the mismatch, when the substrate-film combination is cooled down to room temperature an isotropic in-plane tension will be induced in the film. This in-plane tension is expected to give rise to PMA since CFO has negative magnetostriction [6, 25]. Here the lattice mismatch between substrates-films is not considered since a layer of amorphous silicon dioxide (SiO₂) is formed due to oxidation of Si surface.

Table 4.4: Remanant magnetization (M₀) and coercivity (H₀), and differences in remanant magnetization (ΔM₀) and coercivity (ΔH₀) between the in-plane and out-of-plane hysteresis loops

<table>
<thead>
<tr>
<th>Samples</th>
<th>Out-of-plane</th>
<th>In-plane</th>
<th>ΔM₀=</th>
<th>ΔH₀=</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M₀⊥ (emu/cm³)</td>
<td>H₀⊥ (Oe)</td>
<td>M₀∥ (emu/cm³)</td>
<td>H₀∥ (Oe)</td>
</tr>
<tr>
<td>CFO1</td>
<td>88.12</td>
<td>1985</td>
<td>64.52</td>
<td>2488</td>
</tr>
<tr>
<td>CFO2</td>
<td>92</td>
<td>1348</td>
<td>46.9</td>
<td>591</td>
</tr>
<tr>
<td>CFO3</td>
<td>188</td>
<td>2583</td>
<td>59</td>
<td>1843</td>
</tr>
<tr>
<td>CFO4</td>
<td>107</td>
<td>1381</td>
<td>37.04</td>
<td>1223</td>
</tr>
<tr>
<td>CFO5</td>
<td>117</td>
<td>2194</td>
<td>106.03</td>
<td>5001</td>
</tr>
<tr>
<td>CFO6</td>
<td>98.7</td>
<td>1591</td>
<td>81.8</td>
<td>2678</td>
</tr>
</tbody>
</table>

Magnetic properties of thin films are influenced by a variety of parameters such as film thickness, crystalline structure, composition, and surface/interface roughness. Specifically, surface/interface roughness influence magnetic properties such as magnetic moments, magnetic anisotropy, coercivity, magnetic domain structure, and motion, etc. [26-31]. The decrease of perpendicular magnetic anisotropy in CFO1, CFO6 and in-plane anisotropy in CFO5 is due to the rougher surface of these films [32]. The roughness of the surfaces can affect domain wall motion because domain walls in thin magnetic films interact with the top and bottom surface of the film [33]. The domain wall will always seek to minimize its total area, and so will stick where the sample is thinnest i.e., the surface roughness due to microscopic film thickness variation induced domain wall pinning [23, 33]. The presence of big particles at the surface observes in AFM image (figure 4.2); cause microscopic variation in thickness in the films. The pinning makes the domain wall
motion more difficult, thus resulting in the enhancement of the in-plane coercivity in CFO1, CFO5 and CFO6 samples.

4.3.3 Electrical property:

Figure 4.6: Variation of resistivity and log $\rho$ with temperature for CFO films.

To understand electrical transport properties of CFO thin films, grown by two different techniques, the temperature dependent resistivity has been studied and figure 4.6 shows the results measured in the temperature range of 300K – 400K. The resistivity is very high of the order of $10^5$-$10^7$ $\Omega$-cm at room temperature. The resistivity decreases with increasing temperature which reflects the semiconducting behavior. As discussed in chapter 3, since localized electrons are present in ferrites
and the electrical conduction is by hopping mechanism involving electron exchange between ions of the same element present in more than one valence state and distributed randomly over crystallographically equivalent lattice sites. In the present case electronic conduction takes place by hopping between Fe$^{2+}$ and Fe$^{3+}$ ions present at octahedral (B) sites [34]. When the temperature is raised, the hopping rate is enhanced thereby drift mobility increases. The increase in the drift mobility of the charge carriers which are thermally activated upon increasing the temperature led to the decrease in resistivity with temperature.

The plots of log $p$ vs $10^3/T$ for all the specimens are given in figure 4.6 (b). The activation energies are obtained by fitting the Arrhenius relation given in equation 3.8. Table 4.5 listed the surface roughness, resistivity and activation energy of CFO films. The resistivity and activation energy is higher for the films with high surface roughness. The presence of scattering sites such as point defects, impurities, grain boundaries, rough surfaces and interfaces hinders the motion of charge carriers. Thus the rough surface reduces the hopping rate between Fe$^{2+}$ and Fe$^{3+}$ ions therefore resistivity increases with the increase of surface roughness.

**Table 4.5: Variation of resistivity and activation energy with surface roughness.**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Surface roughness (nm)</th>
<th>Resistivity ($\Omega\cdot$cm)</th>
<th>Activation energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFO1</td>
<td>5.42</td>
<td>$1.4\times10^7$</td>
<td>2.77</td>
</tr>
<tr>
<td>CFO2</td>
<td>1.1</td>
<td>$4.5\times10^6$</td>
<td>2.65</td>
</tr>
<tr>
<td>CFO3</td>
<td>0.64</td>
<td>$3.1\times10^6$</td>
<td>2.56</td>
</tr>
<tr>
<td>CFO4</td>
<td>0.65</td>
<td>$1.6\times10^6$</td>
<td>2.58</td>
</tr>
<tr>
<td>CFO5</td>
<td>12.41</td>
<td>$2.7\times10^7$</td>
<td>2.92</td>
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<tr>
<td>CFO6</td>
<td>9.37</td>
<td>$2.5\times10^7$</td>
<td>2.81</td>
</tr>
</tbody>
</table>
4.4 Conclusion:

Thin films of CFO were grown on quartz and Si (100) substrates by PLD and rf sputtering techniques. XRD study reveals that all the samples except CFO4 which has an amorphous nature, correspond to polycrystalline single phase cubic spinel structure. The films CFO1, CFO2, CFO5, CFO6 are partially textured along (111) direction and CFO3 along (100) direction. Texture evolution of polycrystalline films is explained on basis of minimization of total system energy. Microstructural characterization by AFM technique shows a variation in surface morphology. CFO1, CFO5, CFO6 have a rough surface due to presence of bigger particles at the surface while the films CFO2, CFO3, CFO4 have smooth and flat surface. The hysteresis loops recorded at room temperature for both in-plane and out-of-plane configurations are significantly different suggesting that the films possess magnetic anisotropy. All films possess perpendicular magnetic anisotropy except CFO5 which has in-plane magnetic anisotropy. Magnetic anisotropy and coercivity are greatly affected by surface morphology. Surface roughness also affects the hopping of charge between Fe$^{2+}$ and Fe$^{3+}$ ions. The rough surface enhanced the surface scattering and hence the resistivity.
References:


Chapter 5

Effect of 200 MeV Ag$^{+17}$ Ion Irradiation on the Structural, Magnetic and Electrical Properties of CoFe$_2$O$_4$ Thin Films

This chapter focuses on the modification induced by 200 MeV Ag$^{+17}$ ion irradiation on the structural, magnetic and electrical properties of CFO thin films grown by PLD. The modification is studied with the variation of ion fluence. In addition to fluence dependence, thickness dependence of SHI irradiation effect is investigated.
Chapter 5: Effect of 200 MeV Ag ions irradiation...

5.1 Introduction:

The directional dependence of magnetic properties or anisotropy of magnetic materials is of great importance to both the researchers and technologist to unravel basic magnetic phenomena and exploit them in the design for specific applications [1]. Depending on the type of application, material with high, medium or low magnetic anisotropy will be required. Magnetic thin films with high coercivity and anisotropies are intensively investigated today, in order to satisfy the demand of ever increasing magnetic storage density [1-6]. With large anisotropy, the superparamagnetic limit can be pushed down, and a stable magnetization can be promoted in ultrasmall nanosized magnetic bit, which are needed in advanced media storage for ultrahigh density recording [7]. The magnetic anisotropy can be tuned by varying thickness of film, lattice mismatch between the film and the substrate, composition and processing temperatures [3-5, 7-9, 10-13]. Lisfi et al. [7] have reported reorientation of magnetic anisotropy in epitaxial CFO thin films upon varying the film thickness. The driving force of such a phenomenon is to be the lattice strain. Gao et al. [11] showed that the magnetic anisotropy of epitaxial CFO films grown on SrTiO$_3$ substrates can be reoriented by inserting a thin SrRuO$_3$ buffer layer. The CFO films grown on SrTiO$_3$ substrates have a uniaxial anisotropy with the easy axis perpendicular to the film plane but with the insertion of SrRuO$_3$ buffer layer the easy axis switch in the in-plane orientation. That is associated with a tensile and a compressive strain for the films without and with buffer layer. The switching of magnetic anisotropy from out-of-plane to in-plane associated with a tensile and a compressive strain has also been demonstrated by Dhakal et al. [12] on CFO films grown on MgO and SrTiO$_3$ substrates. Raghunathan et al. [13] studied the variation of perpendicular anisotropy and coercivity in CFO films grown on SiO$_2$/Si (100) with substrate temperature and reported that the perpendicular magnetic anisotropy decreased with decreasing substrate temperature due to the thermal expansion mismatch between the film and the substrate. It has been recently demonstrated that ion irradiation can be used to modify the magnetic anisotropy of thin films and multilayers.
Chapter 5: Effect of 200 MeV Ag ions irradiation...

Swift Heavy Ion (SHI) irradiation is a unique and effective tool which is known to generate controlled defects such as structural strain, point/cluster of defects and columnar defects depending upon the type of ion, energy, fluence and target material [14, 15]. SHI during their passage through material result in excitation and ionization of the atoms by inelastic collisions (called as electronic energy loss, $S_e$) or displace them by elastic collisions (nuclear energy loss, $S_n$). These results in the production of defects in the target and brings modifications in the physical properties of the materials [16]. The shape of the defects introduced by SHI irradiation depends on the $S_e$ of the impinging ions. The defects morphology changes from a cluster of spherical defects to cylindrical defects above a threshold value of electronic energy loss ($S_{eh}$) in magnetic insulators [17, 18]. In complex system like ferrites; where cations reside in two different sublattices, the defects can disturb the arrangement of cations which may result in significant effects on magnetic and electrical properties such as the coercivity, magnetic anisotropy, resistivity etc. The advantage of SHI irradiation is that the properties can be locally control and modify depending upon the electronic energy loss and fluence values in the target materials [16]. The present study focuses on the modification of structural, magnetic and electrical properties in CFO thin films by SHI irradiation using 200 MeV Ag$^{+17}$ ions at different fluences. The thickness dependence SHI irradiation effect on these properties at a specific fluence is also discussed.

5.2 Experimental details:

CFO films were grown on SiO$_2$/Si (100) substrates from CFO target by PLD techniques. The preparation of the target, the mechanism of deposition techniques and details of set-up were discussed in chapter 2. Thin films CFO of thickness about 186 and 41 nm have been grown onto SiO$_2$/Si (100) substrates by PLD method using 284 nm KrF excimer laser with energy 188 mJ and 164 mJ respectively at substrate temperature 500$^\circ$C and oxygen gas pressure of 20 mTorr. The base pressure of the chamber was 6×10$^{-6}$ Torr. The laser repetition rate and the distance between the target-substrate were maintained at 10 Hz, 5 cm respectively. After deposition, it was cooled to the room temperature under same oxygen pressure. 186 nm CFO thin films were irradiated with 200 MeV Ag$^{+17}$ ions beams at different fluences of 5×10$^{11}$
ions/cm\(^2\), 1\times10^{12} \text{ ions/cm}^2 \) and 5\times10^{12} \text{ ions/cm}^2 whereas 41 \text{ nm film at } 5\times10^{12} \text{ ions/cm}^2 at room temperature using 15UD Tandem Accelerator at Inter University Accelerator Center (IUAC) New Delhi, India. The irradiation was performed under high vacuum condition (base pressure 2\times10^{-6} \text{ torr}). Beam current was kept at \sim 0.1 \text{ pA} to avoid heating and beam was focused to a spot of 1 \text{ mm} diameter. Film was scanned over the entire film area using a magnetic scanner. The fluence values were measured by collecting the charge falling on the sample mounted on an electrically insulated sample holder placed in secondary electron suppressed geometry. Ladder current was integrated with a digital current integrator and the charged pulses were counted using scalar counter. The range of such ions in CFO was calculated using SRIM [19] which is \sim 15.53 \text{ \mu m}. This implies that all the ions pass through the film thickness deep into the substrate and therefore the observed irradiation effects are to be analyzed as consequences of ion induced electronic energy transfer.

The structural characterizations were carried out with XRD \( \theta - 2\theta \) scans, Raman Spectroscopy and cross - sectional TEM. Surface morphology and magnetic domain structure were determined by AFM and MFM respectively. Magnetic hysteresis loops were measured at room temperature using a VSM with maximum field of 22 kOe. To understand their electronic structures, XAS and XMCD experiments were performed. The measurements were performed in an ultrahigh-vacuum (UHV = 10^{-10} \text{ mbar}) chamber and magnetic field upto \pm 1 \text{ Tesla} is applied along the easy axis using circularly polarized beam. XAS spectra were recorded in the total-electron-yield (TEY) mode. The degree of circular polarization was 80\%. The DC electrical resistivities were measured by two probe method in the temperature range 300 K-400K.

5.3 Results and discussions:

5.3.1 Fluence dependence SII irradiation effect on CFO thin films:

5.3.1.1 Structural property:

Figure 5.1 shows the XRD pattern of the pristine and irradiated 186 nm CFO thin films and inset showing the shifting of peak position of (400) plane. The pristine film has diffraction peaks which correspond to crystalline cubic spinel structure
Figure 5.1: XRD pattern of the pristine and irradiated CFO thin films and the inset shows the enlarged view of (400) (a) pristine (b) $5 \times 10^{11}$ ions/cm$^2$ (c) $5 \times 10^{12}$ ions/cm$^2$ and (d) target.

(JCPDS File No. 22-1086) with a preferred orientation along (100) as indicated by high relative intensity of (400) peak as compared to (311). The intensity ratio (400)/(311) of the pristine film is 71% which is much larger than corresponding value of 20% for the polycrystalline target. The peaks for pristine thin film are observed to be shifted towards the lower angles with respect to target as shown in the inset of figure 5.1 which indicate the presence of strain. The intensity of all the peaks decreases with increase in fluences value. Partial amorphization of the film created by ion irradiation leads to the decrease of peak intensity. 200 MeV of Ag$^{+17}$ ion corresponds to $S_e \sim 21$ keV/nm was larger than or equal to the threshold (1-20 keV/nm) of formation of homogeneous cylindrical amorphous tracks or columnar amorphization [20-23]. The creation of columnar amorphization is understood based on thermal spike model discussed in chapter 2 [24]. No significant shift was observed in the XRD peak of sample irradiated with low fluence with respect to pristine film; however a shift of diffraction peak towards the higher angle is clearly visible for high
fluence \((5 \times 10^{12} \text{ ions/cm}^2)\) as shown in inset of figure 5.1 which is attributed to the reduction of strain.

![Graph showing Raman Spectra of the pristine and irradiated CFO thin films.](image)

Figure 5.2: Raman Spectra of the pristine and irradiated CFO thin films (a) pristine (b) \(5 \times 10^{11}\) ions/cm\(^2\) (c) \(5 \times 10^{12}\) ions/cm\(^2\) and (d) target.

![Graph showing variation of peak position and intensity with fluence.](image)

Figure 5.3: Variation of peak (a) position and (b) intensity with fluence.
Figure 5.2 shows the Raman Spectra of CFO target and thin films (pristine and irradiated). The cubic spinel structure with $O^7_4$ (Fd3m) space group gives rise to 39 normal modes. Out of these only five modes are Raman active [25, 26]. Raman spectra can be fitted by five Lorentzian curves and found the mode positions to be 307, 470, 520, 622 and 695 cm$^{-1}$ for pristine film. The modes above 600 cm$^{-1}$ correspond to the modes of tetrahedral group that reflects the local lattice effect in the tetrahedral sublattice and those below 600 cm$^{-1}$ represent the modes of octahedral group and reflect the local lattice effect of the octahedral sublattice. The peak at 520 cm$^{-1}$ is due to the silicon substrate. It can be seen that the peak of the target sample is broadened. The pristine film appeared sharper and an obvious blueshift was visible. A blueshift in pristine films was associated with the lattice strain observed in our XRD examinations [25, 27]. The peak positions and the relative intensities were observed to be independent of irradiation and within experimental error at low fluence whereas at high fluence reduced intensity and a small shift of the Raman peak were observed (figure 5.3) due to decrease of strain.

Figure 5.4 show surface morphology seen in AFM images (a-c) and magnetic domain patterns in MFM (d-f) of pristine and irradiated samples. The RMS value of surface roughness was found to be around 1nm for all samples. The MFM images consist of domains with cluster like structure with high contrast for the pristine films. These types of structures are commonly observed in high perpendicular magnetic anisotropy (PMA) materials with large coercivity [3, 7, 10, 28]. Although the cluster like structures persists even with irradiation, the contrast of magnetic image decreases and become less pronounced at the high fluence. The weak contrast of magnetic image implies a small magnetization perpendicular to the film. No stripe structure was observed in these samples. It is important to point out that stripe domains exist in films with low coercivity and pronounced shoulder at nucleation field [7, 28, 29]. To investigate the effect of SHI irradiation in these films especially at the interface, a cross-sectional TEM were carried out. Figure 5.5 displays the high resolution cross-sectional image. These images reveal growth of columnar structure of diameter 20-30 nm across the film and at the interface there is a layer of thickness about 1nm corresponding to SiO$_2$ layer (1 nm) appearing at the CFO/Si interface. At high fluence, the columnar structures start to disappear at the interface.
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Figure 5.4: AFM and MFM images of CFO thin films (a, d) Pristine, (b, e) $5 \times 10^{11}$ ions/cm$^2$ and (c, f) $5 \times 10^{12}$ ions/cm$^2$. 
Figure 5.5: Cross-sectional TEM images of CFO thin film (a) Pristine, (b) $5 \times 10^{11}$ ions/cm$^2$ and (c) $5 \times 10^{12}$ ions/cm$^2$.

3.3.1.2 Magnetic property:

The magnetic hysteresis loops of all the samples were measured by VSM at room temperature in both parallel and perpendicular directions to the film plane and the results are depicted in figure 5.6. As seen in the figure there is a huge difference between in-plane and out-of-plane loops except for high fluence irradiated samples. This clearly suggests that the magnetization easy axis is aligned perpendicular to the film plane. The pristine film has in-plane and out-of-plane coercivity of 1843 and 2583 Oe while remanent magnetization of 59 and 188 emu/cm$^3$ respectively.
Figure 5.6: Magnetic hysteresis loops of CFO thin film (a) Pristine, (b) $5\times10^{11}$ ions/cm$^2$, (c) $1\times10^{12}$ ions/cm$^2$ and (d) $5\times10^{12}$ ions/cm$^2$.

The magnetic anisotropy energy was calculated using the equation

$$K_u = \frac{M_s H_k}{2} \quad (5.1)$$

where $H_k$ is the anisotropy field which can be estimated by extrapolating the in-plane magnetization curve against the out-of-plane magnetization curve [4, 30]. The calculated value of $K_u$ (6.6×10$^6$ erg/cm$^3$) for pristine is larger than the reported magnetocrystalline anisotropy constant (2×10$^6$ erg/cm$^3$) of bulk CFO which indicate the presence of additional magnetic anisotropy constant in this film. Remanant magnetization ($M_r$) and coercivity ($H_c$) in both orientations, differences in remanant magnetization
(ΔM_r) and coercivity (ΔH_c) between the in-plane and out-of-plane hysteresis loops and anisotropy energy (K_u) of the pristine and irradiated samples are listed in table 5.1.

The study of irradiated samples reveals that both magnetizations and coercive field are sensitive to Ag-ions irradiation and exhibits different behaviour depending upon the fluences. The coercivity and magnetization of the out-of-plane loop increases whereas that of in-plane loop is decreased and the anisotropy energy (K_u=8×10^6 erg/cm^3) enhance when a film is irradiated at a fluence 5×10^{11} ions/cm^2. For the film irradiated at fluence 1×10^{12} ions/cm^2, the coercivity as well as magnetization in both directions is decreased. Therefore the anisotropy energy decreases. When the fluence is further increased to 5×10^{12} ions/cm^2, out-of-plane magnetization and coercivity is drastically reduced and the differences between the in-plane and out-of-plane hysteresis loops become less significant as seen in figure 5.6(d). Although in-plane coercivity is increased and is larger than out-of-plane coercivity, similar value of remanent magnetization and saturation field indicates magnetically isotropic. Generally the spin alignment in thin films results from the competition between several uniaxial anisotropies (a) stress anisotropy, induced in the films during the deposition process, the thermal expansion differences or lattice parameter differences between the film and the substrates, (b) the magnetocrystalline anisotropy which is generated by the spin-orbit coupling of the film lattice and (c) the shape anisotropy, due to the difference in the demagnetization factors in the directions parallel and perpendicular to the films [1, 7, 31]. Since the easy axis of magnetization for the CFO is along (100) and this film shows some preferred (100) texture, it is expected to have in-plane anisotropy [1, 13]. On the contrary, we observed PMA in the pristine film as shown in figure 5.6 (a). This may be due to the dominant contribution of stress anisotropy arises due to the associated strain of the film as observed in the XRD and Raman spectra. This strain is developed due to the difference of thermal expansion coefficient of Si substrate (3.5 x 10^{-6} K^{-1}) and the film (1 x 10^{-6} K^{-1}). Such mismatch induced an in-plane isotropic tension in the film when the substrate-film combination is cooled down to room temperature. This in-plane tension is expected to give rise to PMA since CFO have negative magnetostriction [13, 28].
Table 5.1: Remanant magnetization ($M_r$) and coercivity ($H_c$), differences in remanant magnetization ($\Delta M_r$) and coercivity ($\Delta H_c$) between the in-plane and out-of-plane hysteresis loops and anisotropy energy ($K_a$) of the pristine and irradiated samples.

<table>
<thead>
<tr>
<th>CFO thin films</th>
<th>Out-of-plane</th>
<th>In-plane</th>
<th>$\Delta M_r$</th>
<th>$\Delta H_c$</th>
<th>Anisotropy Energy ($K_a$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_{r,\perp}$</td>
<td>$H_{c,\perp}$</td>
<td>$M_{r}$</td>
<td>$H_{c}$</td>
<td>$M_{r,\perp}-M_r$</td>
</tr>
<tr>
<td>Pristine</td>
<td>188</td>
<td>2583</td>
<td>59</td>
<td>1843</td>
<td>129</td>
</tr>
<tr>
<td>$5\times10^{11}$</td>
<td>208</td>
<td>2736</td>
<td>56</td>
<td>1471</td>
<td>152</td>
</tr>
<tr>
<td>$1\times10^{12}$</td>
<td>163</td>
<td>2336</td>
<td>45</td>
<td>1016</td>
<td>118</td>
</tr>
<tr>
<td>$5\times10^{12}$</td>
<td>27</td>
<td>852</td>
<td>31</td>
<td>1856</td>
<td>-4</td>
</tr>
</tbody>
</table>

CFO owing to a spin-orbit stabilized ground state (with unquenched orbital momentum $l_z = \pm 1$) caused by a trigonal crystal field on the Co$^{2+}$ octahedral cations results in a large cubic magnetocrystalline anisotropy. Co L$_{2,3}$-edges XANES and XMCD have been measured at room temperature to understand the distribution of Co$^{2+}$ ions on A and B-sites. Figure 5.7 (a) shows XAS spectra at Co L$_{2,3}$-edges and corresponding XMCD spectra (figure 5.7b) for the pristine and irradiated samples. The major negative peak at 778.8 eV corresponds to the Co$^{2+}$ ions occupying B-sites. In the figure XMCD spectra are normalized by peak at 778.8 eV. Comparing our results with the simulated XMCD spectra for various percentages of Co$^{2+}$ ions site occupancy reported by Hochepie ed. al. shown in figure 5.8, inverse spinel structure is indicated in all the samples [32]. Therefore the change in anisotropy may not be due to change of Co$^{2+}$ ions occupancy.
Figure 5.7: Co L\textsubscript{2,3} edges spectra of pristine and irradiated CFO thin films (a) XANES and (b) XMCD.

Fe L\textsubscript{2,3}-edges XANES and XMCD also measured to investigate the Fe site occupancy and the results is shown in figure 5.9. The XMCD L\textsubscript{3} region shows two negative peaks at 707.7 eV and 709.55 eV corresponding to the Fe\textsuperscript{2+} and Fe\textsuperscript{3+} ions occupying B-sites, a positive peak at 708.8 eV relates to Fe\textsuperscript{3+} ions at A-sites [32, 33]. The XMCD spectra are normalised to the peak 709.55 eV correspond to Fe\textsuperscript{3+} ions at B-sites for comparison. It is clear that there is greater concentration of Fe\textsuperscript{2+} ions at A-sites in sample irradiated at low fluence as compared to the pristine and lower concentration at high fluence samples. However, there are no reports cited in the literature to the best of search where anisotropy changes with Fe\textsuperscript{3+} ions occupancy. There may be some internal structure distortion or local ordering as any change in site occupancy of Fe\textsuperscript{3+} ions should accompanied that of Co\textsuperscript{2+} ions.
Figure 5.8: Variation of theoretical XMCD spectra at Co L$_{2,3}$ edges versus Co$^{2+}$ site occupancy.

Figure 5.9: Fe L$_{2,3}$ edges spectra of pristine and irradiated CFO thin films (a) XANES and (b) XMCD.
O K-edge XANES is used to further investigate the change in in cation-anion bonding and the variation in the site occupancies. O K-edge XANES for pure irradiated samples is given in figure 5.10. The O K-edge probes the unoccupied states with the O 2p symmetry due to the dipole selection rules, which arises mainly from the hybridization of O 2p states with the different states of neighboring atoms, and the 3d states of Fe and Co. The well resolved doublet peaks 529.6 eV and 529.3 eV in the spectrum arise from the covalent or hybridization mixing of O 2p states with 3d states of Fe ions and are assigned as low lying t_{2g} and e_{g} bands with energy separation 10Dq \sim 1.6 eV occurring due to crystal field splitting of the 3d level of the Fe ion [34]. There is variation in the intensity of t_{2g} and e_{g} peaks which suggest the change of site occupancy of Fe ions after irradiation.

![Figure 5.10: O K-edges XANES spectra of pristine and irradiated CFO thin films.](image)

From the above investigation, the modification of magnetic properties of CFO thin films with irradiation could be due to microscopic structural changes or induced defects in the films. The enhancement of PMA at low fluence can be attributed to pinning of domain wall at cylindrical defect sites caused due to ion bombardment. The pinning of a domain wall by spherical defects is independent of the orientation of the domain wall but this is not the case of cylindrical defects. A wall which is parallel
to and whose motion is towards the defects get pinned when it interact with the defects as it is in a minimum energy state. However, a wall which lies perpendicular to the defect will not be pinned as it will always be the same [18, 35]. The anisotropic nature of domain wall pinning at the defect sites during its course of motion result in the increase of anisotropy when such defects are introduced in the samples. As the fluence increases, the density of defects is increased. There will be overlapping of the defect zones which weaken the pinning effect and lead to decrease in the anisotropy. At high fluence, besides weakening of pinning effect, we observe a reduction of strain as observed from XRD and Raman study and destruction of columnar structure near the interface from X-TEM micrograph. This factors leads to decrease of stress anisotropy which results in isotropic behaviour of magnetic properties.

5.3.1.3 Electrical property:

The electrical resistivities were measured as function of temperature in the temperature range of 300 to 400 K and the results are as shown in figure 5.11 (a). The trend of changes of resistivity of the samples with temperature is typical of semiconductors in the sense that the resistivity decreases with the increase in temperature. Figure 5.11 (b) shows the temperature dependence of resistivity as log $\rho$ versus $10^3/T$. It is observed that the resistivities approximately follow the Arrhenius relation given in equation 3.8. The variation of resistivity at 300K and activation energy with irradiation and increasing fluence value are shown in table 5.2.

Table 5.2: Resistivity at 300K and activation energy of pristine and irradiated CFO thin films.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Resistivity (Ω-cm)</th>
<th>Activation energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>$3.1 \times 10^6$</td>
<td>2.56</td>
</tr>
<tr>
<td>$5 \times 10^{11}$</td>
<td>$8.4 \times 10^7$</td>
<td>3.08</td>
</tr>
<tr>
<td>$1 \times 10^{12}$</td>
<td>$1.4 \times 10^8$</td>
<td>3.12</td>
</tr>
<tr>
<td>$5 \times 10^{12}$</td>
<td>$2.1 \times 10^8$</td>
<td>3.26</td>
</tr>
</tbody>
</table>
Figure 5.11: (a) Resistivity vs temperature plots for pristine and irradiated CFO thin films (b) Corresponding logarithmic resistivity as a function of $10^3/T$.

Pristine CFO films are highly insulating with room temperature resistivity of 3 MΩ-cm. The resistivity of the CFO thin films increases almost one order of magnitude at the irradiation fluence of $5 \times 10^{11}$ ions/cm$^2$. The resistivity further increases by an order with the increase of irradiation fluence to $1 \times 10^{12}$ ions/cm$^2$. However, further increase of irradiation fluence up to $5 \times 10^{12}$ ions/cm$^2$, there is increase of resistivity but within the same order. The observed increase in the resistivity with irradiation may be due to the presence of defects in the irradiated samples and degradation of crystallinity [36]. As discussed in the preceding two
chapter that the electrical conduction is due to hopping mechanism involving electron exchange between ions of the same element present in more than one valence state and distributed randomly over crystallographically equivalent lattice sites [37]. The defects sites act as a scattering center for the charge carriers and hindered the hopping process thereby increasing the resistivity.

5.3.2 Thickness dependence SHI irradiation effect on CFO thin films:

In this section, thickness dependence SHI irradiation effect on CFO thin films is investigated. To study the effects, we have irradiated 186 nm and 41 nm CFO thin films by 200 MeV Ag$^{+17}$ ions at a fluence of $5 \times 10^{12}$ ions/cm$^2$. The structure, magnetic and electrical transport properties of the samples before and after the irradiation had been characterized to understands the modifications made by SHI irradiation.

5.3.2.1 Structural property:

![Figure 5.12: XRD pattern of pristine and irradiated CFO thin films (a) 186 nm (b) 41 nm.](image)
Figure 5.12 shows representative XRD patterns of pristine and irradiated CFO thin film of thickness 186 nm and 41 nm. The diffraction peaks of both the pristine films represent a textured crystalline structure with pure spinel phase. The (100) and (222) texture in 186 nm and 41 nm CFO thin films were briefed in chapter 4. Further, the results of XRD indicate that the effect of SII irradiation is different for the 186 nm and 41 nm CFO thin films. In 186 nm film, the intensity of peak decreases drastically after irradiation. However, there is only a slight decrease of diffraction peak intensity in the 41 nm film after irradiation.

The AFM images (a-d) and the corresponding magnetic domain patterns in MFM (e-h) of pristine and irradiated samples are shown in figure 5.13. There is no significant changes in the surface morphology of the irradiated 186 nm thin film [figure 5.13 (a, b)], however, a drastic reduction in the contrast of magnetic image is observed [figure 5.13 (e, f)] due to the weakness of the out-of-plane component of anisotropy. On the other hand, the magnetic image [figure 5.13 (g,h)] for both the pristine and irradiated 41 nm thin films is similar whereas the ditch and dike structure is found to have spread throughout the film in the irradiated sample [figure 5.13 (e, d)]. The rms value of surface roughness increases from 1.10 nm to 2.09 nm after irradiation.
Figure 5.13: AFM and MFM images of CFO thin films of 186 nm (a, e) Pristine, (b, f) $5 \times 10^{12}$ ions/cm$^2$ and 41 nm (c, g) pristine, (d, h) $5 \times 10^{12}$ ions/cm$^2$. 
5.3.2.2 Magnetic property:

![Graphs showing magnetic hysteresis](image)

Figure 5.14: Magnetic hysteresis of CFO thin film of 186 nm (a) Pristine, (b) $5 \times 10^{12}$ ions/cm$^2$ and 41 nm (c) pristine, (d) $5 \times 10^{12}$ ions/cm$^2$.

In order to understand the thickness dependence SHI irradiation effect on magnetic properties of CFO films, VSM studies were performed to achieve magnetic hysteresis loops in both perpendicular and parallel directions to the film planes. As seen in figure 5.14 (a, c), both pristine films exhibit good hysteresis behaviors with PMA. After irradiation, the magnetization and coercivity of 186nm is drastically reduced and the differences between the in-plane and out-of-plane remanent magnetization become insignificant. Moreover, both the hysteresis loops become well saturated at around similar field which indicate the isotropic magnetic property. This transition from anisotropic to isotropic behavior was discussed in section 5.3.1.2.
However, in the case of 41 nm film, the magnetization and coercivity is observed to enhance slightly upon irradiation retaining the anisotropy. Table 5.3 list the remanant magnetization ($M_r$), coercivity ($H_c$) in both orientations, and differences in remanant magnetization ($\Delta M_r$) and coercivity ($\Delta H_c$) between the in-plane and out-of- plane hysteresis loops.

The irradiation induced thickness dependent disparity in the magnetic properties of CFO films is attributed to the damage created by the energetic ions is thickness dependent. The columnar track produced by an energetic ion is straight and its diameter is very small for some initial small thickness. As the energetic ion keeps losing energy with increasing thickness, the diameter of the columnar track increases and linearity of the track is not maintained. Therefore, with increasing thickness, the probability for the scattering and collision of highly charged energetic ion with the matter is large in different directions so it creates a columnar defect with large diameter [38]. This leads us to infer that the effect generated by energetic ion passing through the film will be greater for thicker film as compared to that of thinner film as observed in our XRD examination.

Table 5.3: Remanant magnetization ($M_r$) and coercivity ($H_c$), and differences in remanant magnetization ($\Delta M_r$) and coercivity ($\Delta H_c$) between the in-plane and out-of- plane hysteresis loops.

<table>
<thead>
<tr>
<th>CFO thin films</th>
<th>Out-of-plane</th>
<th>In-plane</th>
<th>$\Delta M_r$</th>
<th>$\Delta H_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_{r\perp}$ (emu/cm$^3$)</td>
<td>$H_{c\perp}$ (Oe)</td>
<td>$M_{r\parallel}$ (emu/cm$^3$)</td>
<td>$H_{c\parallel}$ (Oe)</td>
</tr>
<tr>
<td>186 nm</td>
<td>188</td>
<td>2583</td>
<td>59</td>
<td>1843</td>
</tr>
<tr>
<td>186 nm (Irr)</td>
<td>27</td>
<td>852</td>
<td>31</td>
<td>1856</td>
</tr>
<tr>
<td>41 nm</td>
<td>92</td>
<td>1348</td>
<td>46.9</td>
<td>591</td>
</tr>
<tr>
<td>41 nm (Irr)</td>
<td>100</td>
<td>1714</td>
<td>46</td>
<td>898</td>
</tr>
</tbody>
</table>
5.3.2.3 Electrical property:

The thickness dependence of SHI irradiation effect on electrical transport properties is studied by measuring resistivity as a function of temperature in the range 300K to 400K and the results are depicted in figure 5.15. Table 5.4 listed the resistivity at 300K and activation energy of the pristine and irradiated CFO thin films. The resistivity increases by two order of magnitude after irradiation for 186 nm thin film. Interestingly, in the 41 nm thin film, in the whole temperature range investigated; there is only a slight increase in resistivity but within same order with irradiation. The observed thickness dependence of SHI irradiation effect on resistivity is due to larger diameter of columnar defects in the thicker film than thinner one which provides larger scattering sites.

![Graphs showing resistivity vs temperature and logarithmic resistivity vs inverse temperature for pristine and irradiated CFO thin films.](image)

Figure 5.15: Resistivity vs temperature plots for pristine and irradiated CFO thin films and corresponding logarithmic resistivity as a function of $10^3/T$ of thickness (a, b) 186 nm and (c, d) 41 nm.
Table 5.4: Resistivity at 300K and activation energy of 186nm and 41 nm (pristine and irradiated) CFO thin films.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Resistivity (Ω-cm)</th>
<th>Activation energy (eV)</th>
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</thead>
<tbody>
<tr>
<td>186 nm</td>
<td>3.1×10^6</td>
<td>2.56</td>
</tr>
<tr>
<td>186 nm (Irr)</td>
<td>2.1×10^5</td>
<td>3.26</td>
</tr>
<tr>
<td>41 nm</td>
<td>4.5×10^6</td>
<td>2.65</td>
</tr>
<tr>
<td>41 nm (Irr)</td>
<td>6.4×10^6</td>
<td>2.67</td>
</tr>
</tbody>
</table>

5.4 Conclusion:

CFO thin films of thickness 186 nm and 41 nm were deposited on SiOx/Si substrate by PLD process and study the effect of 200 MeV Ag^{+17} ion beam at three different fluences in 186 nm film and the dependence of thickness at a particular fluence. XRD measurement confirms the textured crystalline spinel structure of both the pristine films. Magnetization measurements performed at room temperature shows that the magnetic easy axis is aligned perpendicular to the film for pristine sample. The anisotropy increases at fluence 5×10^{11} ions/cm² and then decrease with the further increase of fluence. At fluence 5×10^{12} ions/cm², anisotropy ceases and becomes isotropic. XANES and XMCD measurement demonstrate that Co^{2+} ion occupancy remains unchanged after irradiation which excludes change in anisotropy due to Co^{3+} ions occupancy. The increase of anisotropy at low fluence is due to anisotropic domain wall pinning but at higher fluence weakening of pinning effect leads to decrease of anisotropy. XRD, Raman and TEM studies have revealed that reduction of strain and destruction of columnar growth results in transition from anisotropic magnetic behavior to isotropic at high fluence. The resistivity increases with increasing fluence value due to the scattering of charge carrier at the defects. The thickness dependence of SHI irradiation effect study reveals that the SHI irradiation have a great impact on thicker film due to the damage created by the energetic ions is thickness dependent. From the present study, it can be inferred that magnetic and electrical properties of CFO thin films can be tuned or modify by varying the fluence of SHI irradiation and thickness of the film.
References:


Chapter 5: Effect of 200 MeV Ag ions irradiation...


Chapter 6

Effect of 200 MeV Ag$^{+17}$ and 100 MeV O$^{+7}$ Ions Irradiation on the Structural and Magnetic Properties of CoFe$_2$O$_4$ Thin Films

This chapter presents the effect of 200 MeV Ag$^{+17}$ and 100 MeV O$^{+7}$ ions irradiation on the structural and magnetic properties of CFO thin films grown by rf sputtering techniques on Si substrate. This work was carried out to understand the role of electronic energy loss, $S_e$ in the modification of the structural and magnetic properties.
6.1 Introduction:

The magnetic and electrical properties of thin films are extremely sensitive to structural and morphological changes (grain shape and size, surface roughness) or presence of defects and imperfections. [1-8]. The physics of defects creation by swift heavy ions on magnetic insulators [9–15] and other materials [16–18] have been extensively studied since last two decades. There are a few reports on the SHI irradiation on different ferrite systems (nanoparticles/thin films) [19-21]. Ghosh et. al. studied the damage creation in nanocrystalline Li–Mg ferrite thin films by using 190 MeV Au$^{14+}$ ions and reported the significant changes in magnetic and electrical properties [15]. Sharma et. al. investigated the effect of 200 MeV Ag$^{15+}$ ion irradiation on structural and magnetic properties and irradiation induced texturing of Mn$_{95}$Mn$_{95}$Fe$_2$O$_4$ ferrite thin film and shown that irradiation can modify the structural and magnetic properties [19, 20]. Dogra et. al. explored the influence of 190 MeV Ag ion irradiation on the structural and magnetic properties of NiMn$_{0.05}$Ti$_{0.05}$Mn$_{0.05}$O$_{4.5}$ (x = 0.0, 0.2) ferrite thin film and reported that for undoped film NiMn$_{0.05}$Fe$_{1.95}$O$_4$, the magnetization has decreased with the ion fluence. In case of thin film of NiMn$_{0.05}$Ti$_{0.2}$Mn$_{0.2}$Fe$_{1.99}$O$_4$ the saturation magnetization value increases up to certain fluence and decreases at higher fluence [21]. So far, the irradiation studies were reported on mixed and doped ferrites. In that case, it is difficult to interpret the effect of irradiation because doping provides complications in the system. Therefore, it is better to choose a simple system in which the effects due to doping and other complications are negligible. As mentioned in the previous chapter, the ion beam irradiation effects depend on the energy of ion beams and ion species. In this chapter, the effect of 200 MeV Ag$^{+17}$ ions and 100 MeV O$^{17+}$ ions irradiation on the structural and magnetic properties of CFO thin films prepared by rf sputtering method is presented.

6.2 Experimental details:

CFO thin films were grown on SiO$_2$/Si (100) by rf sputtering. The pressure of the sputtering gas, argon, was 20 mTorr without additional reaction oxygen gas. The samples were annealed in 700°C for 3 h in O$_2$ atmosphere. The films were irradiated with 200 MeV Ag$^{+17}$ and 100 MeV O$^{17+}$ ion beams with different fluences of $5 \times 10^{11}$
ions/cm² and $5 \times 10^{12}$ ions/cm² at room temperature using 15UD Tandem Accelerator at IUAC, New Delhi. All the experimental conditions of ion beam irradiation were similar to the previous experiments. The crystal structure and phase purity of the samples were analyzed by XRD and Raman spectroscopy. The measured thickness of the film is 60 nm. The magnetic hysteresis loops of the samples were measured by VSM at room temperature.

6.3 Results and discussions:

6.3.1 Structural property:

![XRD pattern of the pristine and 200 MeV Ag⁺ ions irradiated CFO thin films.](image)

Figure 6.1 (a): XRD pattern of the pristine and 200 MeV Ag⁺ ions irradiated CFO thin films.
Figure 6.1 (b): XRD pattern of the pristine and 100 MeV O$^{+7}$ ions irradiated CFO thin films.

The XRD pattern of the pristine and 200 MeV Ag$^{+17}$ ions and 100 MeV O$^{+7}$ ions irradiated CFO thin films are shown in figure 6.1 (a) and (b) respectively. The pristine film has diffraction peaks which corresponds to crystalline cubic spinel structure with a preferred orientation along (222) indicated by high intensity ratio of (222)/(311) diffraction peak. The intensity of all the peaks decreases with 200 MeV Ag$^{+17}$ ions irradiation due to partial amorphization of the films. The amorphization due to 200 MeV of Ag$^{+17}$ ions irradiation have been discussed in the previous chapter. But from the figure 6.1 (b), it is clearly seen that the films irradiated by 100 MeV O$^{+7}$ ions have no amorphization even though the (222) texturing has reduced. The possible reason is the low $S_e$ value. For 100 MeV oxygen ions, the typical values of $S_e$ and $S_n$
as calculated by TRIM/SRIM are 116.6 eV/ Å and 6.59×10⁻² eV/ Å respectively. These values are much smaller than the threshold value of electronic energy loss, (Se)th, [22-25], required for creating columnar amorphization along the ion track. The possible effects of ion irradiation with 100 MeV O⁺ ions could be the formation of few point/cluster defects.

Figure 6.2 (a): Raman Spectra of the pristine and 200 MeV Ag⁺ ions irradiated CFO thin films.

Raman spectra of the pristine, 200 MeV Ag⁺ ions and 100 MeV O⁺ ions irradiated CFO thin films are depicted in figure 6.2. The Raman peak positions are in good agreement with those reported in the literature for CFO [26]. The intensity of Raman peak of 200 MeV Ag⁺ ions irradiated films at fluence 5×10¹¹ ions/cm² are of similar value but at the high fluence, 5×10¹² ions/cm² irradiated sample, some of the peaks disappear and the intensity is significantly reduced. This further confirms the amorphization of the film. In the 100 MeV O⁺ ions irradiated films just as in the case of XRD, there is only slight decrease in intensity of the peak due to presence of some point/cluster defects.
Figure 6.2 (b): Raman spectra of the pristine and 100 MeV O\(^{17}\) ions irradiated CFO thin films.

Figure 6.3 shows surface morphology (2D & 3D) of pristine and irradiated samples. The surface of pristine film consist of small grains (average size 50 nm) among which some bigger (average 120 nm) particles are distributed unevenly forming pillars like pattern (also discussed in chapter 4). The value of rms roughness of the films was evaluated for 5×5 \(\mu\)m\(^2\) by Nanoscope Software. The rms value of surface roughness was found to be 10.11 nm for pristine samples. After irradiation at fluence 5×10\(^{11}\) ions/cm\(^2\), there is growth of grains and surface roughness increase to 10.99 nm. With further increase in fluence to 5×10\(^{12}\) ions/cm\(^2\), the grains are almost uniform and the surface roughness decreases to 9.78 nm. The little variation in surface morphology is also observed in 200 MeVAg\(^{17}\) ions irradiated CFO thin films grown PLD (presented chapter 5). However, the surface morphology of the 100 MeV O\(^{17}\) ions irradiated films is drastically different from the pristine film. The surface roughness of the films increases drastically and is found to be 24.39 nm. The grains
Figure 6.3 (a): AFM images of the pristine and 200 MeV Ag$^{+7}$ ions irradiated CFO thin films.
Figure 6.3 (b): AFM images of the pristine and 100 MeV O$^{17}$ ions irradiated CFO thin films.
are agglomerated and the topographies of the surfaces appear to be like hills and valleys structure. The observed effects are attributed to the lateral displacement of the local surface layer arises as a sequence of cumulative effects of ion impacts. According to Chicoine et. al. [27] lateral mass transport takes place in the system due to momentum transfer of the atoms leading to such drastic changes. Ghosh et. al. [28] observed severely damaged with some deep ditches (holes) or channel-like features after irradiation with 100 MeV Ag ions. With increase of fluence to $5 \times 10^{12}$ ions/cm$^2$, there is growth of the grains and the size of the hills as well as surface roughness decreases. The modified surface features indicate the evolution of rough surface at comparatively lower fluence and surface diffusion as smoothing mechanism at higher fluence. The smoothing mechanism is also evidenced from the reduction in the value of rms surface roughness.

6.3.2 Magnetic property:

The magnetic hysteresis loops were measured at room temperature both parallel and perpendicular directions to the film plane and the results are depicted in figure 6.4. In the pristine film, the value of remanant magnetization ($M_r$) and coercivity ($H_c$) are different along the two directions suggesting that the films possess magnetic anisotropy. However, the difference in remanant magnetization is small. Therefore the anisotropy is weak. Table 6.1 list the remanant magnetization ($M_r$) and coercivity ($H_c$) in both orientations, and differences in remanant magnetization ($\Delta M_r$) and coercivity ($\Delta H_c$) between the in-plane and out-of-plane hysteresis loops from Figure 6.4. Irradiation with 200 MeV Ag$^{17}$ ions at fluence $5 \times 10^{11}$ ions/cm$^2$ slightly enhanced the overall magnetic parameters due to the slight modifications in structure. However, with the increase of irradiation fluence to $5 \times 10^{12}$ ions/cm$^2$, the film transformed to complete isotropic behavior. This observation is somewhat similar to which we observed in CFO thin films grown by PLD presented in chapter 5. Anisotropic to isotropic change is not observed in the 100 MeV O$^{27}$ ions irradiated films. However, films irradiated at a fluence $5 \times 10^{11}$ ions/cm$^2$ have in-plane coercivity and magnetization larger than the out-of-plane coercivity and magnetization which are a clear indication of in-plane magnetic anisotropy. This modification is mediated by the modifications of surface morphology. In-plane magnetic anisotropy for rough
surface film was also observed in CFO thin films grown on quartz substrate by rf sputtering (presented in chapter 4).

Figure 6.4 (a): Magnetic hysteresis loops of the pristine and 200 MeV Ag$^{17}$ ions irradiated CFO thin films.
Figure 6.4 (b): Magnetic hysteresis loops of the pristine and 100 MeV O^{17} ions irradiated CFO thin films.
Table 6.1: Remanant magnetization ($M_r$), coercivity ($H_c$) and differences in remanant magnetization ($\Delta M_r$) and coercivity ($\Delta H_c$) between the in-plane and out-of-plane hysteresis loops

<table>
<thead>
<tr>
<th>Samples</th>
<th>Out-of-plane</th>
<th>In-plane</th>
<th>$\Delta M_r$</th>
<th>$\Delta H_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_{r\perp}$</td>
<td>$H_{c\perp}$</td>
<td>$M_{r\parallel}$</td>
<td>$H_{c\parallel}$</td>
</tr>
<tr>
<td>Pristine</td>
<td>98.7</td>
<td>1591</td>
<td>81.8</td>
<td>2678</td>
</tr>
<tr>
<td>Ag $5 \times 10^{11}$</td>
<td>104.3</td>
<td>1741</td>
<td>84.63</td>
<td>3046</td>
</tr>
<tr>
<td>Ag $5 \times 10^{12}$</td>
<td>15.8</td>
<td>322</td>
<td>13.8</td>
<td>372</td>
</tr>
<tr>
<td>O $5 \times 10^{11}$</td>
<td>103.6</td>
<td>1728</td>
<td>123.56</td>
<td>3217</td>
</tr>
<tr>
<td>O $5 \times 10^{12}$</td>
<td>100.86</td>
<td>1593</td>
<td>92.93</td>
<td>2805</td>
</tr>
</tbody>
</table>

6.4 Conclusion:

To understand the role of ion species and energy, irradiation experiments with 200 MeV Ag$^{17}$ ions and 100 MeV O$^{17}$ ions were performed on the rf sputtered deposited CFO thin films and the results indicate strong dependence of structural and magnetic properties on the electronic energy loss. XRD and Raman spectroscopy revealed the partial amorphization of the CFO thin films when irradiated with 200 MeV Ag$^{17}$ ions while the surface morphology study uncover the severe effect on the surface of the film when irradiated with 100 MeV O$^{17}$ ions resulting in modifications of magnetic properties. Present studies showed that irradiation induced surface defects can be controlled by choosing a suitable $S_e$ value and fluences which in turn control the magnetic properties.
Chapter 6: Effect of 200 MeV Ag and 100 MeV O ions irradiation...

References:

Chapter 7

Conclusion and Future Perspective

This chapter presents an overview of experimental results obtained from present research and scope of future work.
Chapter 7: Conclusion and future perspective

7.1 Conclusion:

This thesis investigated the possibility of engineering various physical properties especially structural, morphological, electrical and magnetic properties by doping of In in CFO nanoparticles, growing CFO thin film on different substrates and under different conditions and finally introducing defects after processing by SHI irradiation. Major findings are summarized in this chapter.

(1) Single phase nanoparticles of CoFe$_2$O$_4$ and CoIn$_{0.15}$Fe$_{1.85}$O$_4$ have been prepared by citrate – gel method. The average grain size decreases whereas porosity and specific surface area increase in the doped sample. Magnetization measurement shows reduction in saturation magnetization and enhancement in the coercivity. The temperature dependence of dc resistivity follows the Arrhenius relation; resistivity, activation energy and dielectric constant are higher while dielectric loss and conductivity reduced for the doped sample. The modification in magnetic and electrical properties is attributed to the decrease of grain size and increase of porosity. The present investigations clearly point out that the physical properties CFO depends strongly on the morphological features like grain size, microstructure etc for low percentage of doping.

(2) Thin films of CFO were grown on quartz and SiO$_2$/Si (100) substrates by PLD and rf sputtering techniques from a stoichiometric CFO target prepared by citrate-gel method. Three films coded as CFO1, CFO2, CFO3 were grown by PLD and another three CFO4, CFO5, CFO6 by rf sputtering. XRD study reveals that the films CFO1, CFO2, CFO5, CFO6 are partially textured along (111) direction and CFO3 along (100) direction. Texture evolution of polycrystalline films is explained on basis of minimization of total system energy. Morphological study state that CFO1, CFO5, CFO6 have a rough surface due to presence of bigger particles at the surface while the films CFO2, CFO3, CFO4 have smooth and flat surface. Room temperature hysteresis loops showed the anisotropic nature of magnetic properties of the films. All the films possess perpendicular magnetic anisotropy except CFO5.
which has in-plane magnetic anisotropy. The extent of anisotropy was different and depends on the surface morphological conditions. The smooth and flat surface films possess a clear perpendicular magnetic anisotropy whereas the films with rough surface had in-plane coercivity greater than the out-of-plane coercivity. The study infers that magnetic anisotropy and electrical transport properties can be tailored by engineering surface morphology.

(3) CFO thin films of thickness 186 nm and 41 nm deposited on SiO$_2$/Si substrate by PLD process were irradiated with 200 MeV Ag$^{+17}$ ion beam at three different fluences 5×10$^{11}$ ions/cm$^2$, 1×10$^{12}$ ions/cm$^2$ and 5×10$^{12}$ ions/cm$^2$ in 186 nm film and 41 nm at a 5×10$^{12}$ ions/cm$^2$ fluence. Magnetization study reveals that the magnetic easy axis is aligned perpendicular to the film for pristine sample. The anisotropy increases at fluence 5×10$^{11}$ ions/cm$^2$ but at fluence 5×10$^{12}$ ions/cm$^2$, anisotropy ceases and becomes isotropic. The increase of anisotropy at low fluence is due to anisotropic domain wall pinning due to columnar defects but at higher fluence weakening of pinning effect leads to decrease of anisotropy. XRD, Raman and TEM studies have revealed that reduction of strain and destruction of columnar growth results in transition from anisotropic magnetic behavior to isotropic at high fluence as XMCD demonstrate the unchanged Co$^{2+}$ ions occupancy. The resistivity increases with increasing fluence value due to the scattering of charge carrier at the defects. The thickness dependence of SHI irradiation effect study reveals that the SHI irradiation on 186 nm thin film have drastic changes in the structure, magnetic and electrical while these properties remain nearly unchanged in 41 nm film.

(4) The role of ion species and energy is investigated with 200 MeV Ag$^{+17}$ and 100 MeV O$^{+7}$ ions irradiations performed on the rf sputtering deposited CFO thin films. XRD and Raman spectroscopy reveals the partial amorphization of the CFO thin films when irradiated with 200 MeV Ag$^{+17}$ ions while the surface morphology study uncover the severe effect on the surface of the film.
when irradiated with 100 MeV O$^{17}$ ions. Magnetic hysteresis loop measured in in-plane and out-of-plane orientation unravel anisotropic to isotropic transition in 200 MeV Ag$^{17}$ ions irradiation at fluence $5 \times 10^{12}$ ions/cm$^2$ whereas PMA to in-plane magnetic anisotropy in 100 MeV O$^{17}$ ions irradiated at fluence $5 \times 10^{11}$ ions/cm$^2$. Our studies and the results showed strong dependence of structural and magnetic properties on the electronic energy loss and irradiation induced surface defects can be controlled by choosing a suitable $S_p$ value at different fluences.

7.2 Future perspective:

As demonstrated in this work, defects induced by SHI irradiation can modify and tuned the magnetic anisotropy. However, there are still more research is needed on magnetic anisotropy for practical applications:

(1) Attempts can be made to develop perpendicular recording media due to the increasing demand of ultra high density storage media with the miniaturization of the devices. However the development of these media may encountered difficulties since high density recording requires a bit dimension of only a few nanometer in diameter and thus precise control of media microstructure, especially grain size, superparamagnetic instability etc. High anisotropy and coercivity value can overcome the thermal instability expected from such nanoscale ferromagnetic particles. The high magnetic anisotropy can be developed with underlayers structure, introducing strains and defects.

(2) Exchange anisotropy or exchange bias (EB), which arises due to the exchange interaction at the interface when a ferromagnetic (FM) materials is in contact with antiferromagnetic (AFM) materials is fascinating area of research. EB is one of the most striking discoveries in magnetism. Currently exchange bias is used to pin the reference layer in spin valve read heads and Magnetic Random Access Memory (MRAM) memory circuits based on the gaint magnetoresistance (GMR) or magnetic tunneling effect. Up to now, various theoretical approaches have been put forward since its discovery but
theoretical microscopic understanding of the EB phenomenon is still lacking inspite of its technological applications. Therefore, experimenting and identify the missing link between experiment and theory need to be focussed.

(3) Ions irradiation is an excellent experimental tool to control microstructure and to modify surface or interfaces. Future studies may be focused on using a range of ions, energy and fluence can be bombarded on the above mention system and tuned the desired properties.
LIST OF PUBLICATIONS
PAPERS PUBLISHED IN INTERNATIONAL REFEREED JOURNALS:


6. "Ferromagnetism and adiabatic to non-adiabatic switching process in $La_{0.33}Sr_{0.67}Mn_{1.5}Fe_5O_8$ (0≤x≤0.02) manganite"; Hifal Ahmed, Shakeel Khan, Wasi Khan, Razia Nongjai, Imran Khan, J. Magn. Magn. Mater., 368, 273 (2014).

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2. "Surface morphology, magnetic anisotropy and resistivity in CoFe₂O₄ thin films"; Razia Nongjai, Shakeel Khan, S. Annapoorni, V. V. Siva Kumar, K. Asokan. (Submitted to Applied Surface Science).

3. Thickness dependence swift heavy ion irradiation effect on structural, magnetic and electrical properties of CoFe₂O₄ thin films”; Razia Nongjai, Shakeel Khan, S. Annapoorni, K. Asokan. (Submitted to Advanced material letters).

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PAPERS PUBLISHED IN NATIONAL / INTERNATIONAL CONFERENCES / SYMPOSIA:


LIST OF PAPERS PRESENTED IN NATIONAL/INTERNATIONAL
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2. "Frequency Dependence of Ac Conductivity and Impedance Spectroscopy of Ni_{0.7}Mg_{0.3}Fe_{2-x}Al_{x}O_{4} (0.0 \leq x \leq 0.5) Ferrite Nanoparticles"; Razia Nongjai, Dr. Shakeel Khan, Dr. K. Asokan, Hilal Ahmad, Imran Khan, National conference Aligarh Nano I at in A.M.U., Aligarh held on 26th - 27th March, 2011. Organised by Department of Applied physics, A.M.U., Aligarh.


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Delhi held on October 9-12, 2012. Organised by Inter-University Accelerator Centre, New Delhi.


8. “Thickness dependence swift heavy ion irradiation effect on structural and magnetic properties of CoFe$_2$O$_4$ thin films”; Razia Nongjai, Shakeel Khan, S. Annapoorni, K. Asokan, International Conference on Swift Heavy Ions in Materials Engineering and characterization (SHIMEC 2014) at Inter-University Accelerator Centre, New Delhi held on October 14-17, 2014. Organised by Inter-University Accelerator Centre, New Delhi.