Magnetic Studies on $CoFe_2O_4$Thin Films Prepared by Spin Coating method

Dissertation submitted in partial fulfillment of the requirements for the Degree of

MASTER OF SCIENCE

By

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CERTIFICATE

This is to certify that the project entitled "**Magnetic Studies on $CoFe_2O_4$ Thin Films Prepared by Spin Coating method**" being submitted by Miss Neeru Rani in the partial fulfillment of requirement for the award of the degree of Masters of Science in the **School of Physics and Material Science, Thapar university, Patiala**, is an original work carried out under the supervision of **Dr. Puneet Sharma, SPMS** and no part of this project has been submitted for award of any other degree by me.

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Place:Patiala
Date: 17th July, 2017

This is to certify that the above mentioned statement of the student is correct to the best of my knowledge and belief.

Date: 17th July, 2017

Thapar University, Patiala

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Neeru Rani

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ABSTRACT

Cobalt ferrite thin films were prepared by sol gel spin coating method. The effect of annealing temperature and film thickness on structural and magnetic properties was investigated. The chosen annealing temperature were 700 °C, 800 °C, 900 °C, 1000 °C and film thickness were varied from 0.40 µm to 0.70µm. As the annealing temperature increased the coercivity decreased. Saturation magnetization increased with increasing annealing temperature. At 1000 °C film showed relatively high saturation magnetization (284.5emu/cc) and low coercivity (293.5Oe). The magnetic hysteresis loops for perpendicular and parallel to the planes of substrate are same. The surface morphology investigated by field emission scanning electron microscope for films fabricated at different temperature and different thickness.

Ferrites are compound of mixed oxide of iron and one or more other metals which has ferrimagnetic properties. Ferrites are regarded as good magnetic materials because of their higher resistivity, lower cost, easy manufacturing and favorable magnetic properties. They are extensively used as permanent magnets, transformer core, high frequency application and microwave devices [1].

Ferrites are classified on the basis of their magnetic behavior and crystal structure.

1.1. Types of ferrites

1.1.1 Based on their magnetic behavior

- Soft Ferrite
- Hard Ferrite

(a) Soft ferrite: Soft ferrite materials are those that can be easily magnetized and demagnetized. They exhibit narrow hysteresis loop, high permeability, low coercivity (H_c) and high saturation magnetization [2, 3].

(b) Hard ferrite: Hard ferrite materials are those that cannot be easily magnetized and demagnetized. These are also known as permanent magnets. They show rectangular hysteresis loop, high coercivity (H_c).

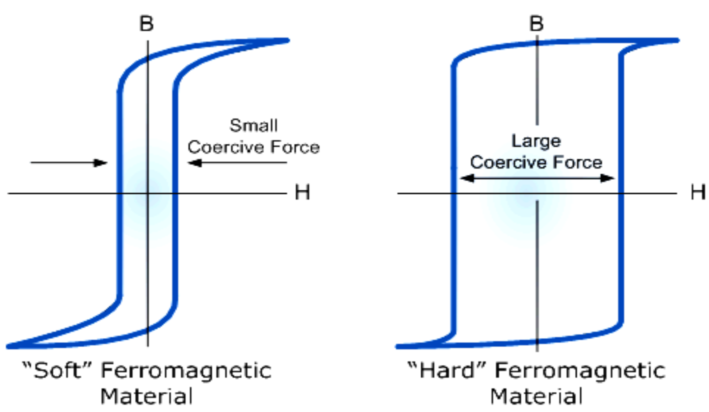


Fig.1.1 Hysteresis loop for soft and hard ferrite materials.

1.1.2Types of ferrite based on crystal structure

- Spinel ferrite
- Garnet ferrite
- Hexagonal ferrite
- Ortho ferrite

Table 1.1 Classification of ferrite

Types	Crystal Structure	General formula	Example
Spinel	Cubic	$A^{II}Fe_2O_4$	A^{II}= $CoFe_2O_4$, $NiFe_2O_4$
Garnet	Cubic	$A^{III}{}_3Fe_5O_{12}$	A^{III}=Y,Sm,Eu,Gd,Tb,Dy,
Magnetoplumbite	Hexagonal (M-Type) (Y-Type) (W-Type)	$A^{II}Fe_{12}O_{19}$ $A_2Me_2Fe_{12}O_{22}$ $AMe_2Fe_{16}O_{27}$	A^{II}=$BaFe_{12}O_{19}$,$SrFe_{12}O_{19}$ Me = Fe^{+2}, Ni^{+2}, Mn^{+2}etc.
Orthoferrite	Perovskite	$A^{III}FeO_3$	A^{III}=Y,Sm,Eu,Gd,Tb,Dy

The present work is based on preparation of $CoFe_2O_4$ spinel ferrites therefore, the few important characteristics of spinel ferrites is described below.

1.2. Spinel Ferrite

Spinel ferrites are soft ferrites and are also known as cubic ferrite. Magnetite (Fe_3O_4) is most popular and important magnetic spinel. General chemical formula for spinel ferrite is $A^{II}Fe^{III}{}_2O_4$ where A^{II} represent divalent metal ions as shown in Table 1.1.

1.2.1 Crystal Structure of spinel ferrites

Spinel ferrite lattice consist of closely packed oxygen ions in cubic configuration. These closely packed oxygen ions forms two different interstitial sites i.e. tetrahedral (A sites) and octahedral (B sites).One unit cell of spinel ferrite consists of 32 oxygen atoms that have 64 tetrahedral sites and 32 octahedral sites. If, tetrahedral (A) sites and octahedral (B) sites both will be occupied by divalent metal ion (+2 valence) and trivalent metal ion (+3 valence) then structure will not be electrically neutral because positive charge becomes more than negative charge. So divalent metal ions are 8A out of 64 tetrahedral sites and trivalent metal ions are 16B out of 32 octahedral sites [4-6].The magnetism in this type of structure is due to the super-exchange mechanism between two metal cations. Crystal structure of spinel ferrite is as shown in fig 1.2:

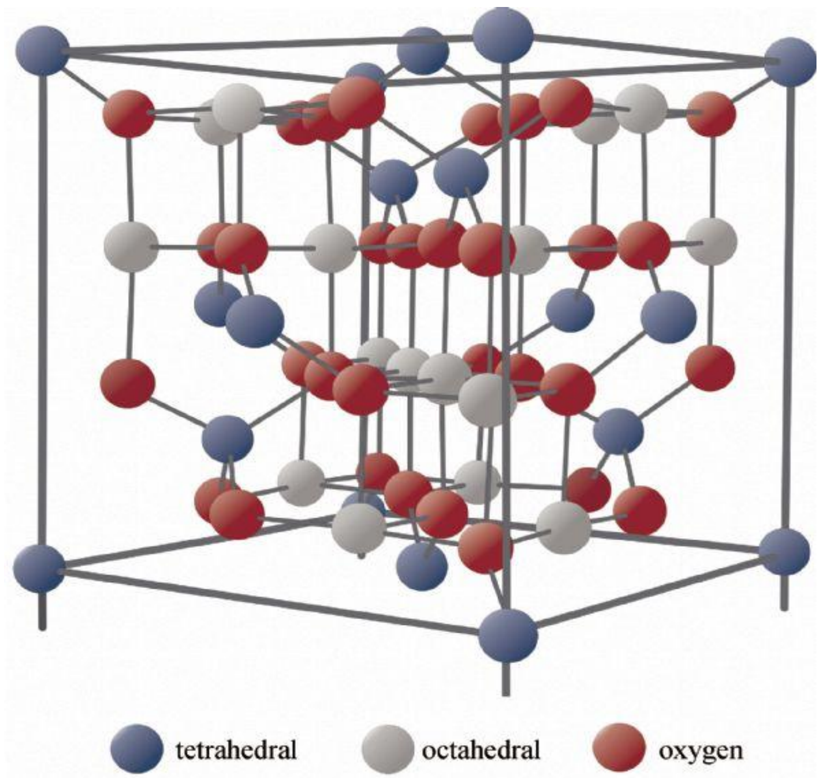


Fig.1.2 Crystal structure of spinel ferrite.

1.2.2Types of Spinel ferrite

Spinel ferrites are classified into three types on the basis of their ion distributions in the octahedral and tetrahedral sites.

1) Normal spinel ferrite
2) Inverse spinel ferrite
3) Mixed spinel ferrite

1.2.2.1 Normal spinel ferrite

In this, spinel divalent metal ions occupy the tetrahedral sites (A sites) while the trivalent metal ions occupy the octahedral sites (B sites). General formula for normal spinel ferrites is $A^{tet}[B_2]^{oct}O_4$.$CdFe_2O_4$ and $ZnFe_2O_4$ are the examples of normal spinel ferrites, in which divalent cations Cd^{2+} and Zn^{2+} are occupied on the tetrahedral sites (A sites) and trivalent cations (Fe^{3+}) are occupied on the octahedral sites (B sites).

1.2.2.2Inverse spinel ferrite

In this spinel ferrite, all divalent cations(8A) and half of trivalent cations(8B) occupy the octahedral sites and remaining half of trivalent cations (8B) occupy the tetrahedral sites. So, cations on octahedral sites have equal proportion of the divalent cations and trivalent cations. General formula for inverse spinel ferrite is $(B)^{tet}[AB]^{oct}O_4$. $CoFe_2O_4$ and $NiFe_2O_4$ are examples of inverse spinel ferrites, in which Co^{2+} and Ni^{2+}divalent cations occupy the octahedral sites(B sites).

1.2.2.3 Mixed spinel ferrite

Mixed spinel ferrite lies between the normal and inverse spinel ferrite. General formula for mixed spinel ferrite is $(A_{1-X}B_X)^{tet}$ $[B_{2-X}A_X]^{oct}O_4$. $MgFe_2O_4$ and $CuFe_2O_4$ are examples of mixed spinel ferrites, in which mixed valance of different ions occupy both tetrahedral and octahedral sites.

Apart from bulk and nanopowders these spinal ferrites have wide application in thin films. These thin films can be deposited by various techniques that are listed below:

1.3Deposition techniques for ferrite thin films

1) Spin Coating
2) Pulsed laser deposition(PLD)
3) RF sputtering
4) Liquid Phase Epitaxy (LPE)
5) Electron-beam Evaporation

1.3.1 Spin Coating

Spin coating is simple and common technique for deposition of thin films on substrates. The thickness of the deposited films can vary from few nanometers to few microns. This technique has vast application in the field nanotechnology and organic electronics. In this technique firstly, the pre-cleaned substrate is ultra-sonicated in order to remove any dust particles. Then it is placed in the spin coating machine. Coating of substrate at high speed rotation is done. Spin speed is the important factor in the spin coating technique for defining the range of thickness.

- **Applications**

  This technique can be used for coating of very small substrate (few mm square) or flat panel TV (meter or more in diameter). Substrates of different materials such as organic semiconductors, photo resistors, synthetic metals, insulator etc. can easily be coated by using this technique.

- **Advantages**

1) Spin coating is the simple and easy technique for achieving thin and uniform films.
2) Due to high spin speed ability, the airflow leads to faster drying, which in turn results in high uniformity of film at both nano and macroscopic scales.

- **Disadvantage**

1) Spin coating is a single substrate process so it is slow process as compare to others.
2) During coating on a substrate, only 10% of the material remains on substrate while remaining all flips off the side and is wasted.

1.3.2 Pulsed Laser Deposition (PLD)

Pulsed laser deposition (PLD) is a thin film deposition (specially a physical vapor deposition, PVD) technique where a high-power pulsed laser beam is focused inside a vacuum chamber in order to strike a target that is to be deposited. The material is vaporized from the target (in a plasma plum)which get deposited as a thin film on a substrate (such as a silicon wafer facing the target).When the laser pulse strikes the target, energy is first converted into electronic excitation and then, later into chemical, mechanical and thermal energy which results in evaporation, plasma formation, ablation and exfoliation. The emitted species spread out into the surrounding vacuum in the form of plume that contains many energetic species including molecules, ions, electrons, atoms, particulates, molten globules and clusters before depositing on the hot substrate.This process can be done in ultra-high vacuum or in the presence of a background gas, such as oxygen which is commonly used while depositing oxides [9].

- **Advantages**

1) This technique is simple, as in this a laser beam vaporizes the target surface which results in deposition of film with the same concentration as the target.

2) Different materials can be deposited in a wide variety of gases above a large range of gas pressures.
3) Film can be deposited in 10 or 15 minutes.
4) This is cost-effective as single laser can provide various vacuum systems.

1.3.3 RF sputtering

Radio frequency (RF) sputtering is a technique that is used to synthesize thin films that are widely used in semiconductor and computer industry. Similar to direct current (DC) sputtering, this technique includes running an energetic wave through an inert gas to create positive ions. The target material, which will ultimately become the thin films coating, is struck by these ions and broken up into a fine spray that covers the substrate, the inner base of thin films. RF sputtering differs from DC sputtering in the voltage, system pressure, sputter deposition pattern, and ideal type of target material [10-13].

During the sputtering process, the target material, substrate, and RF electrodes begin in a vacuum chamber. After that, the inert gas, which is usually argon, neon, or krypton depending on the size of target material's molecules, is directed into the chamber. The RF power source is then turned on, sending radio waves through the plasma to ionize the gas atoms. Once the ions begin to contact the target material, it is broken into small pieces that travel to the substrate and begin to form a coating.

- **Applications**

1) Sputtering is used broadly in the semiconductor industry to produce thin films of different materials in integrated circuit processing.
2) For optical applications, sputtered thin film is used as antireflection coating on glass.
3) As, substrate temperature is low, so sputtering is used in thin film deposition on transistors.
4) In the fabrication of CDs and DVDs sputtering is used to deposit the metallic layer.

1.3.4 Liquid Phase Epitaxy (LPE)

Liquid phase epitaxy (LPE) is a process to grow semiconductor crystal layers on solid substrates. This is carried out at the temperatures just below the melting point of the deposited semiconductor. In the melt of another material semiconductor is dissolved. At the conditions of equilibrium between deposition and dissolution, the deposition of semiconductor crystal is done slowly on the substrate. The equilibrium conditions mainly depend on the concentration and temperature of the dissolved semiconductor in the melt. By the forced cooling of the melt we can control the growth of the layer from the liquid phase. Impurity introduction can be reduced.

In the liquid phase epitaxy, in the case of horizontal tool, the substrate and melt both are brought in the contact to substrate by sliding boat system. When this process is completed then the next melt is brought in the contact with next substrate. By this way, it become possible to grow multi-layer stacks. By addition of dopants we can dope the film. Liquid phase epitaxy is used to produce compound semiconductors. By liquid phase epitaxy we can produce very thin, high quality and uniform layers of films.

1.3.5 Electron Beam Physical Vapor Deposition (EBPVD)

Electron Beam Physical Vapor Deposition (EBPVD) is a form of physical vapor deposition. In physical vapor deposition a target anode is bombarded with an electron beam given off by a charged tungsten filament under high vacuum. This electron beam produces atoms from the target to transforms into gaseous phase. These atoms then precipitate into solid form which results in coating of substrate in the vacuum chamber.

1.4. Properties of Spinel Ferrite

Spinel ferrites are technologically significant class of magnetic oxides. The spinel ferrites possess good electrical, structural and magnetic properties. The magnetic and electrical properties of spinel ferrites are strongly dependent on deposition techniques, chemical composition, sintering temperature and cations distribution.

1) Spinel ferrites have high resistivity with low eddy current losses.
2) They show less electrical conductivity (10^2 to 10^{-11} Ohm^{-1} cm^{-1}) as compared to other magnetic materials and therefore they are largely used at microwave frequencies. The conductivity in these ferrites is because of the existence of metal ions (Me^{3+}) and Fe^{2+}.
3) They possess low coercivity, high saturation magnetization and low remanence magnetization.

A lot of research has been carried out on spinel ferrite thin films but some important work done in this field has been summarized below:

Tuchiya et al. in 1992 prepared the spinel ferrite MFe_2O_4 (M=Co, Ni, Mg) films by sol-gel process using dip-coating technique on silica glass plate using glycerol, formamide and metal nitrates as raw materials . At 400ºC, spinel type ferrite crystalline phase appeared and with increasing the temperature, the crystallinity increased. It was observed that coercive force increased with increasing temperature till 600ºC to 700ºC then decreased by increasing temperature, as spinel type ferrite after heat treatment 600ºC to 700ºC showed single magnetic domain structure.

In 1998, Cheng prepared thin films of cobalt ferrite by sol-gel method and observed that the grain size and morphology depends on the annealing temperature of thin films. Thin films of cobalt ferrite have lower magnetization as compare of bulk phase. Also, Thin films of cobalt ferrite films has high narrow distribution and high quality surface of grain sizes were observed above the annealing temperature of 770ºC for one hour. High coercive forces, nanometer grains and reasonable magnetization used for reducing media noise and recording application. In 1998 the same year Lee studied that fabricate cobalt ferrite layers were fabricated on thermally oxidized silicon wafers by sol-gel method. Their structural and magnetic properties were determined by XRD, AFM and VSM. Mossbauer spectroscopy was used to analyze the crystallization temperature of Co ferrite thin films. A single phase spinel structure of Co ferrite films without any crystallite orientation was observed above 450 °C annealing temperature. Above 650ºC annealing temperature the observed grain size was 30nm and surface roughness was less than 3nm. However, coercivity strongly depends on annealing temperature. At temperature 550ºC, no significant difference in magnetic parameters at applied perpendicular and parallel fields to planes in the films.

In 1999, Peng reported that films of cobalt spinel ferrite prepared by sol-gel method on monocrystalline silicon (100) substrates at low temperature. Processing parameters including calcinations temperature and composition of coating solution were optimized by XRD and AFM studies. The obtained films were annealed at 630-679ºC for 1 h possess well crystallized spinel structure and high quality surface. The substitution of foreign ions in preparation of cobalt ferrite gives a more convenient performance.

In 2000, Duque reported that $CoFe_2O_4$ films were prepared by using coconut water as a solvent. In these magnetic properties of $CoFe_2O_4$ films were investigated by SQUID magnetometer. $CoFe_2O_4$ films have single phase structure annealed at 700°C and there is no significant difference in magnetic properties by applying external fields in parallel or perpendicular to the plane. Small grain size is useful for recording media and reducing media noise. In 2000 Cheng reported that Co-RE (RE= rare earth) composite oxides films prepared by sol-gel method on quartz substrate. Co-RE films studies magneto-optical effects and microstructure were carried out. Results showed that Co-RE composite films have smaller grain size as comparedto Co ferrite thin films. Doping of Lu or Yb with cobalt ferrite increases the magneto-optical rotations 350-420 nm which is used in magneto-optical recoding media. In 2000, Hu reported that epitaxial $CoFe_2O_4$ films play an important role for understanding the magnetic properties and anomalous magnetic behavior which can be explained on the basis of lattice distortion and cations distributions. Magnetic anisotropy balances between the magneto crystalline anisotropy and strain anisotropy. Varying the cobalt cations distributions in the octahedral and tetrahedral sites and strain state of films is able to tune the magnitude of magnetic anisotropy and symmetry. In 2003, Sathaye reported that cobalt ferrite films prepared by modification of spin coating method. In this method of modification common inorganic chemicals are used as starting material to grow thin films of ternary/binary oxides. Deposit cobalt ferrite films by this technique are more useful as compared to other wet chemical techniques because of formation of films at low temperature and small particle size.In 2005, Pramanik reported that thin film of $CoFe_2O_4$was prepared by sol-gel process using aqueous solution of $CoCl_2.6H_2O$ and $FeCl_3.6H_2O$. Film was deposited on oxidized silicon-substrate by spin-coating technique and calcinations temperatures varying from 700to 1100°C. Film thickness was restricted in range of 400-500 nm. Films showed multi-phases of CoO, $CoFe_2O_4$ and α-Fe_2O_3 at lower temperatures, when temperature is increased formation of $CoFe_2O_4$ phase was also increased. In the production of cobalt ferrite films, great role of the composition of solution in mol% and film containing 50 mol% of Co^{2+} show $CoFe_2O_4$ mono-phase. Magnetic properties and surface morphology were studied by the vibrating sample magnetometer (VSM) and scanning electron microscope (SEM).

In 2006, Mohallem reported that composite thin films of cobalt ferrite $CoFe_2O_4/SiO_2$ prepared by sol-gel method using dip coating technique. Metallic nitrates were used as precursor for ferrite and tetraethylorthosilicate (TEOS) as a precursor for silica. Magnetic properties were investigated by SQUID magnetometer. Superparamagnetic behavior was observed at below blocking temperature and at room temperature. In 2008, Araujo reported that $CoFe_2O_4$ thin films prepared by pulsed laser ablation on Si (001) substrates with different deposition temperatures (T_{Dep}=25-600°C) of substrates. When the deposition temperature was low the films were composed of a mixture of cubic spinel structure with $CoFe_2O_4$ and antiferromagnetic oxides of iron and cobalt with FeO and CoO stoichiometry. When the deposition temperature increased then FeO and CoO were strongly decreased, so when deposition temperature (T_{Dep}=600°C) 600°C films were not presents a mixture it's mainly a polycrystalline $CoFe_2O_4$. By increasing deposition temperature exchange field decreased and magnetic properties coercivity and remanence ration increased. This all due to the content FeO and CoO reduced and $CoFe_2O_4$ phase of thin films. In 2009, Phua reported that cobalt ferrite thin films were deposited by spray pyrolysis with isothermal annealing. As-deposited film shows crystallization peak at 375°C when isochronal heating 20°C/min by differential scanning calorimetry and shows amorphous like characteristic by X-ray diffraction. Isothermal post annealing at various temperature from 400-700°C for 2 h forms the spinel structure and crystallization of films. After annealing thickness remains constant by scanning electron microscope (SEM) analysis and when annealing temperature is high the layered granular structure appears. As deposited films and after annealing at higher temperature there is increase in crystallinity, crystallization peak as well as in the coercivity and saturation magnetization.

In 2011, Raghunathan observed that thin films of cobalt ferrite (CFO) were prepared by pulsed laser deposition (PLD) technique on Si(100)/SiO_2 substrates at substrate temperature (T_{DEP}) of 250°C and varying oxygen pressures (P_{O2}) 0.67 to 6.7 Pa. the effect of P_{O2} on phase mixture, magnetic properties, and crystal structure and deposition rate was observed. It was observed that thin films of cobalt ferrite by varying the P_{O2} (oxygen pressure) and lower substrate temperature open a window of these thin film materials can be used in MEMS device and in multilayer sensors. In 2012 Kumbhar reported that thin films of cobalt ferrite ($CoFe_2O_4$) were prepared by simple chemical method using alkaline bath having Fe^{2+} and Co^{2+} ions, on stainless steel substrate. By scanning under electron microscope, formation of nano-flakes was observed.

These nano-flakes have high surface area which can be used for super capacitance applications. The impedance and charge-discharge study encouraged this fact.

In 2012, Sun reported that polycrystalline cobalt ferrite thin films were prepared by sol-gel method using glucose as an additional agent. Magnetic and structural properties as well as morphology and annealing temperature investigated in detail. Single phase spinel structure of cobalt ferrite obtained at lower temperature 300ºC as compared to traditional ceramic method temperature (about 500-600ºC). By this method, it was concluded that cobalt ferrite films have a small crystallite size (10 nm) at 300ºC and films annealed at 600ºC crystallite size (42nm) remains small. So using glucose $CoFe_2O_4$ thin films shows very small particle size (32nm) annealed at 400ºC and excellent magnetic properties which is more useful for information storage applications. In 2013, Khodaei reported that thin films of perfectly (111)-oriented $CoFe_2O_4$ were produced by pulsed laser technique on Si/Pt (111) substrates while substrate temperature 600^0C. Based on magnetic and structural properties oxygen pressure was found to be 10 mTorr. The film produced at 1 mTorr has the highest magnetization and (111)-orientation degree. Because of thermal residual strain which depend upon thickness of films were under in-plane tensile stress. It was established that the (111)-oriented $CoFe_2O_4$ thin film demonstrates the strong in-plane magnetic anisotropy which outcomes from orientation as well as the stress-induced magnetic anisotropy. In 2013, Wei reported that cobalt ferrite thin films were prepared on monocrystalline silicon (100) substrate at low temperatures. Surface morphology and structural properties of deposited films were observed by FESEM and XRD. Surface morphology of films was observed different at different calcination temperature. Results showed that, at 800 °C the magnetic properties of cobalt films were similar as that of powder. In the deposited film the relaxation of stress related with the decrease in coercivity. In 2013, Liu reported that $CoFe_2O_4$ ferrites showing a high curie temperature (T_C>600°C) and large magnetostriction coefficient are good contestants for generate magnetic at nanoscale and with varying potential for magneto electric coupling give a way to fabrication of matrix films. Nanocomposite thin films possessed of a ferroelectric/piezoelectric polymer poly (Vinylidene fluoride co-hexafluoropropene), P(VDF-HFP) and cobalt ferrite nanocrystals (8 to 18nm) were prepared by cast coating and multiple spin coating over a thickness vary of 200nm to 1.6 µm. By all characterization we get the proof of cooperative interaction between the two phases. An increase in saturation magnetization and effective permittivity of $CoFe_2O_4$-P (VDF-HFP) was observed and compared with $CoFe_2O_4$-nonferroelectric polyvinylpyrrolidene film prepared by same method. By this comparison it was observed that CFe_2O_4-P (VDF-HFP) films assigned to magnetostrictive/piezoelectric interaction. In 2015, Mustaqima reported that (111) preferentially oriented thin films of cobalt ferrite prepared by spin coating method on TiO_2/Si/SiO_2/Pt (111) substrates. The thickness of film and post-annealing conditions for cobalt film were varied and Pt/CFO/Pt structures were produced to analyze the resistance switching behaviors. Our results represented that resistance switching absence of forming process is favored to obtain less variation in the set voltage. In place of thicker films, thin films of CFO prepared by two step spin coating provided stable resistance switching behavior with high stable set voltage because the large fluctuation and forming process have been supposed as serious problems for practical application of resistance switching for non-volatile memory devices. In 2015 Chen reported that hetroepitaxial thin films of $CoFe_2O_4$ (CFO) were deposited on MgO (001) substrate with different thickness. Due to the out-of-plane compressive strain, thinner films (<100nm) showed a perpendicular magnetic anisotropy whereas larger shape anisotropy effect was observed in thicker films. XRD analysis showed lattice matching between MgO substrate and $CoFe_2$ films. Annealed films showed a nanopore mushroom structure whereas by TEM analysis investigated that thin films are continuous. Results showed that, by hydrogen reduction we can modify structure and magnetic anisotropy of epitaxial $CoFe_2O_4$. In 2015 Dai reported that polycrystalline thin films of $CoFe_2O_4$ prepared by chemical solution deposition on Si (100) substrate without magnetic annealing. The variations of microstructure, magnetic anisotropy and strain of the films produced by the magnetic annealing are examined. The results appear that grain morphology is varied and film densification is promoted by the magnetic annealing, which can be assigned to the promoting effect on the grain boundary and grain growing. It is observed that after magnetic annealing saturation magnetization and anisotropy of the films were increased. In 2015, Hisamatsu reported that thin films of $CoFe_{3-X}O_4$ (CFO) was prepared on MgO substrate by RF-sputtering technique to develop the interface magnetism and show very large perpendicular magnetic anisotropy, we tried to introduce two different spinel type oxides one is $MgTi_2O_4$ (MTO) and another is $CoCr_2O_4$ (CCO) in between the MgO (001) substrate and CFO films. While both buffer layers were epitaxially produced on MgO (001), CFO films produced on CCO/MgO (001) showed significantly lower magnetization and polycrystalline, whereas the CFO films produced on MTO/MgO (001) magnetization knock down as a function of thickness of the MTO layer. Incredible interdiffusion for Mg and Co analyzed by secondary ion mass spectroscopy.

In 2016, Jha reported that thin films of cobalt ferrite were prepared by pulsed laser deposition on fused quartz substrate. The various parameters oxygen pressure, substrate temperature and magnetic, structural and morphological properties were studied by VSM,XRD and AFM. Film showed the formation CFO along preferred [110] direction at the lower substrate temperature (400^o C) and at higher substrate temperature (800^o) it becomes textured also increasing saturation magnetization and grain size 21 to 46 nm and. Coercivity decreasing with increasing temperature. Saturation magnetization decreased with increasing oxygen pressure (up to 0.4 mbar) and for highest value of oxygen pressure it's increased. Coercivity increased with increasing oxygen pressure (0.2 to 0.4 mbar) and it's decreased for the higher value of oxygen pressure (0.8 mbar). In 2016 Lee reported that thin films of amorphous $CoFe_2O_4$ were deposited on Mgo (001) substrates with different thickness by pulsed laser deposition (PLD) to investigate the correlation between the magnetic properties of films and oxygen vacancies results showed that, as the thickness of film increased saturation magnetization was also increased with decreased in coercivity and oxygen vacancy. In 2016 Bursik reported that highly (111) oriented thin films of $CoFe_2O_4$ and Co_3O_4 were prepared by chemical solution deposition technique on $SrTiO_3$, MgO, Zr $(Y)O_2$ and $LaAlO_3$ substrates and crystallized at 700°C. Structure and morphology of films were investigated by XRD and SEM. While all spinel films show clear out of plane orientation regardless of substrate and in-plane orientation strongly depend on lattice mismatch between substrate and films. In 2017 Tang reported that thin films of CFO prepared by sol-gel method on silicon (001) substrate. High coercivity (H_c) thin films are required in applications. Sol-gel has hindered the preparation of CFO thin films which is the difficulty in achieving the high coercivity thin films. At room temperature remanence ratio (M_r/M_s) , coercivity and maximum magnetic energy product $(BH)_{max}$ have largest values and at same time thickness and annealing temperature effects on $(BH)_{max}$, H_C and M_r/M_s are investigated. Results shows that the residual tensile strain and grain size both are responsible for the variation of M_r/M_s and H_c. These all results give an effective route for development larger area high coercivity thin films on silicon wafers with low cost sol-gel method. In 2017, Kumar reported that thin films of cobalt ferrite deposited by pulsed laser deposition (PLD) on $Si/TiO_2/SiO_2/Pt$ (111) substrate at constant pressure of oxygen 9Pa and temperature of substrate vary from 550 to750^{0}C. By X-ray diffraction and Raman Spectra all films shows single phase (111) preferred orientations. Films deposited at low temperature 550^{o}C and 650^{o}C shows smooth and uniform surface whenever film deposition at higher temperature 750^{o}C shows voids and porosities due to re-evaporation of atoms of films. Results shows increase in out of plane domain size and coercivity and by induced tension decrease in in-plane due to mismatch of thermal expansion film and substrate at higher deposition temperature. In 2017 Zhang reported that deposition of two types of spinel ferrite films $Co_xFe_{3-x}O_4$ and Fe_3O_4 on Ti/Si/SiO_2/Pt (111) substrates using one-step electrochemical deposition technique. Orientation of thin films changed from (111) to (100) by SEM and XRD characterizations with increase in deposition time. In $Co_xFe_{3-x}O_4$ films cobalt content studied by EDS analysis. Ferromagnetic resonance (FMR) behavior of films was studied by the flip-chip method. Results showed that the increased in the applied magnetic field perpendicular or parallel with linearly increase in FMR frequency which indicates that films can be used for tunable frequency devices and wave-absorbing material in RF band. In 2017 Bagade reported that polycrystalline thin films of CFO were prepared by spray pyrolysis technique on quartz substrates. Rietveld refinement analysis were showed polycrystalline nature of thin films with spinel cubic crystal structure and appointed to approximate cations distributions in spinel lattice. Morphology and phase formation study was observed by SEM and FTIR. VSM study confirmed that the moderate coercivity with maximum saturation magnetization was beneficial for manufacturing effective gas sensor. The gas response with respect to different gas concentration, solution concentration, operating temperature was uniformly studied. The obtained films showed that the maximum gas response 70% at 150^{o}C operating temperature and 0.1 M solution concentration.

3.1. Preparation of sample

Following steps are used for preparation of cobalt ferrite ($CoFe_2O_4$) film

1) Preparation of sol
2) Deposition of film
3) Annealing of film

3.1.1 Preparation of Sol using Sol-gel method

Sol for cobalt ferrite thin films was prepared by using sol-gel method. Sol-gel method can be used to prepare fine powder, thin films, fibers, monoliths and microspheres. Fe $(NO_3)_3.9H_2O$ (A.R), $Co(NO_3)_2.6H_2O$ (A.R) and citric acid ($C_6H_{10}O_8$) were dissolved in DI water with continuous stirring. After 2 hours of stirring, ammonia solution was added drop wise in order to adjust the pH level. The pH of the solution was adjusted because the stability of the solution depends upon pH. After addition of ammonia, mixture was again stirred at 70^0C for 1 hour, for getting good viscous solution. Sol used for preparation of Cobalt ferrite film has been shown in fig. 3.1.

Fig. 3.1 Sol for preparation of cobalt ferrite film.

3.1.2 Deposition of film

To deposit the cobalt ferrite films, Al_2O_3 substrate (0.9cm×0.9cm) was ultrasonically cleaned for 30 minutes. Now, the sol was spin coated on the substrate at 3000 rpm for 30 second and this process is repeated to increase the thickness of the film. After each coating film was dried for 10 minutes at 200°C in Muffle furnace. Fig. 3.2 shows the spin coating machine.

Fig.3.2 Spin Coating Machine

3.1.3 Annealing of film

After coating, thin film of cobalt ferrite has been annealed at the different temperatures (700^0-1000^0C) in tubular furnace for 1 hour. Tubular furnace is shown in fig 3.3 As-prepared cobalt ferrite thin film is shown in fig. 3.4.

Fig. 3.3 Tubular Furnace

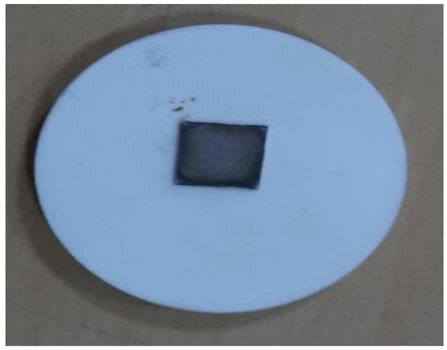
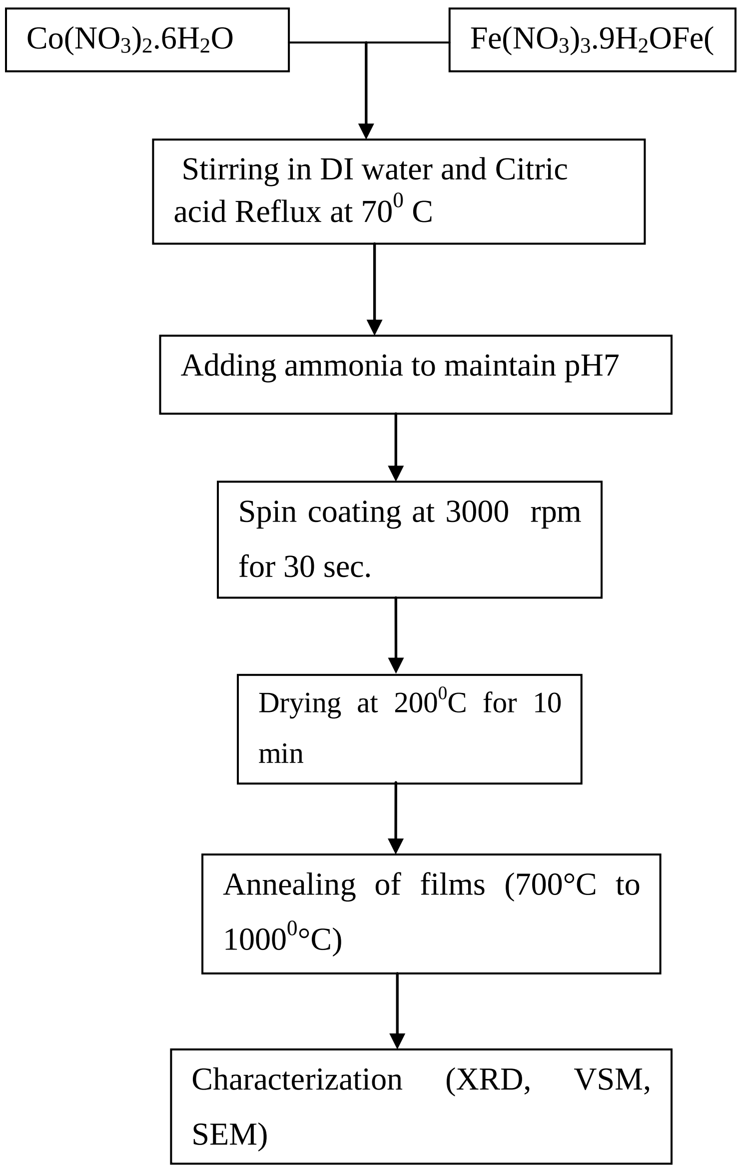


Fig. 3.4 Annealed cobalt ferrite film.

3.2Flow chart for the deposition of cobalt ferrite thin film



4.1 X-ray diffraction (XRD)

Phase analysis of cobalt ferrite thin film and powder has been carried out by using X-ray diffraction method. Fig. 4.1 illustrates the XRD pattern of cobalt ferrite thin film deposited on alumina substrate. No well distinguished peaks of cobalt ferrite were observed due to high intensity of alumina substrate peaks, which suppresses the small intensity cobalt ferrite peaks. Moreover, the diffraction angles of alumina and cobalt ferrite are very close, therefore the diffraction peaks overlaps and are not distinguished. Table 1.1 shows the standard and observed diffraction angle and peak intensity of alumina and cobalt ferrite, which shows the close proximity of diffraction angles.

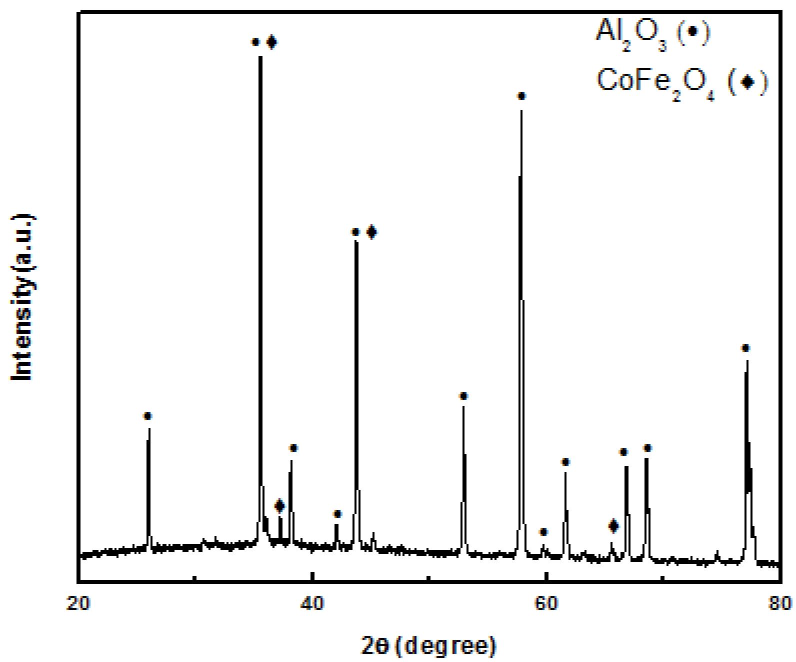


Fig. 4.1 XRD pattern for cobalt ferrite thin film deposited on alumina substrate.

Table 4.1X-ray diffraction peaks.

Observed Peaks		Standard JCPDS (01-075-1862) (Al_2O_3)			Standard JCPDS (03-0864) ($CoFe_2O_4$)		
(2θ)	Intensity	(2θ)	Intensity	(hkl)	2θ	Intensity	(hkl)
25.92	24.15	25.54	67.80	012			
30.61	1.15				30.06	20	220
35.43	84.39						
35.49	100.00	35.10	100.00	104	35.45	100	311
37.14	4.94				37.28	6	222
38.07	15.24	37.73	45.80	110			
41.94	4.54	41.62	0.50	006			
43.63	59.52	43.30	96.10	113	43.47	20	400
52.81	25.54	52.48	47.20	024			
57.75	80.98	57.42	90.90	116			
59.67	2.15	59.67	2.30	211			
61.54	14.82	61.21	8.50	018			
63.27	1.09				62.72	64	440
65.50	2.72				65.70	2	531
66.75	17.73	66.43	34.80	214			
68.43	17.90	68.13	53.20	300			
70.76	0.77	70.32	1.10	125	70.78	2	620
74.60	1.76	74.19	1.30	208			
77.08	37.84	76.75	14.90	1010			
77.16	39.40	77.12	8.60	119			

Since the phase formation of cobalt ferrite is not identified from the XRD of films, therefore cobalt ferrite powder were prepared by using the similar sol-gel method and annealed at 800 ^oC. Fig. 4.2 shows XRD pattern of synthesized cobalt ferrite powder. The well crystalline single phase cobalt ferrite was observed. Therefore, it can be concluded that the deposited film may also possess single phase cobalt ferrite. The lattice parameters have been determined by using following equation:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad (1)$$

The calculated lattice parameter 'a' is 8.31Å and comparable with standard reported value. Crystallite size has been determined by the Scherrer formula:

$$D = \frac{0.9\lambda}{\beta cos\theta} \quad (2)$$

where θ is Bragg's angle, λ is wavelengths of x-rays and β is full width at half maxima and average crystallite size is equal to 48.82 nm.

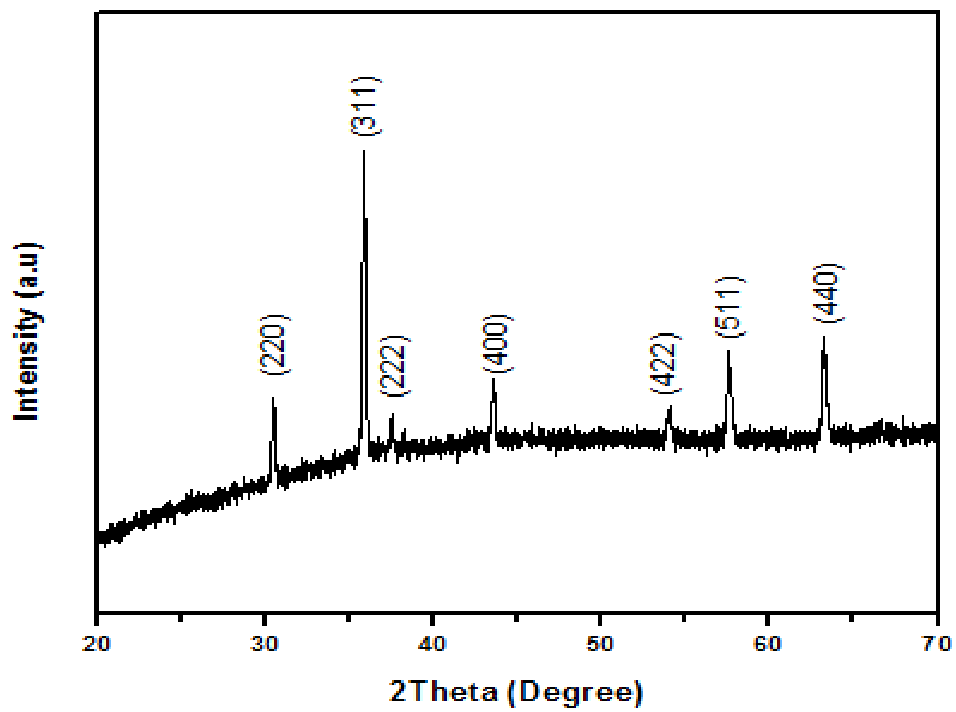


Fig. 4.2XRD pattern for cobalt ferrite Powder

4.2. Magnetic Analysis

Magnetic analysis of synthesized powder and thin film has been carried out by Vibrating Sample Magnetometer (VSM).Fig 4.3 illustrates *M-H* loop of cobalt ferrite powder, annealed at 800^{0}C. A well saturated *M-H* loop of cobalt ferrite powder observed and a characteristic of a soft magnetic materials. Saturation magnetization (M_s), coercivity (H_c) and remanence magnetization (M_r) of $CoFe_2O_4$ powder has been tabulated in Table 4.2.

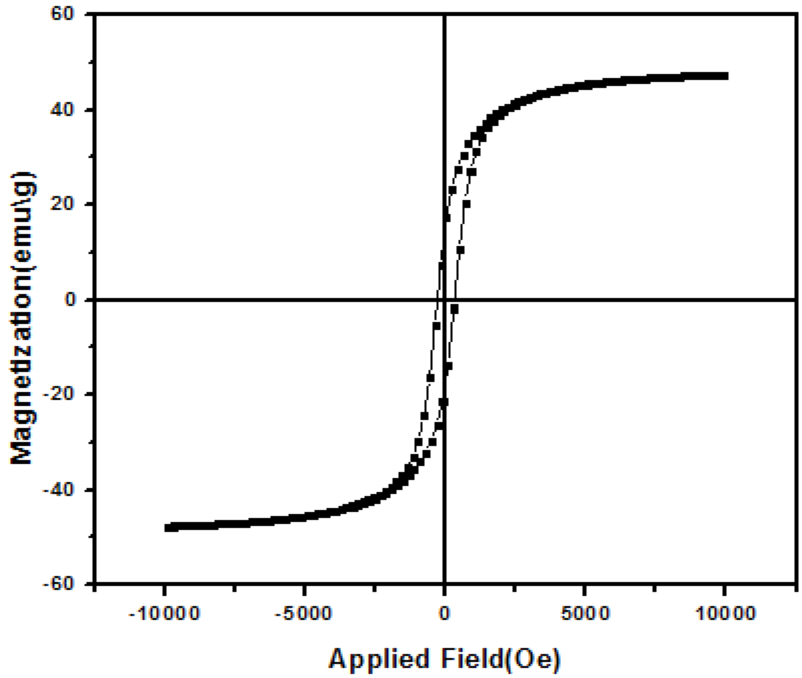


Fig. 4.3*M-H* loop for cobalt ferrite powder annealed at 800°C.

Table: 4.2 Magnetic properties of cobalt ferrite powder

T **(^{o}C)**	$\boldsymbol{M_s}$ **(emu/g)**	$\boldsymbol{M_r}$ **(emu/g)**	$\boldsymbol{H_s}$ **(Oe)**
800	45.2	14.23	306

M-H loops of $CoFe_2O_4$thin film annealed at different temperatures (700°C, 800°C, 900°C, 1000°C) are shown in fig. 4.4.*M-H* behavior of films are found similar to powder. Therefore, it is well confirmed that film contains soft magnetic $CoFe_2O_4$phase.*Ms*and M_r found to increase with annealing temperature and found maximum at 1000°C. Magnetic properties of the films annealed at different temperatures are tabulated in table 4.3. *Hc* has been found to decrease with the annealing temperature, which is due to grain growth of the film with temperature.

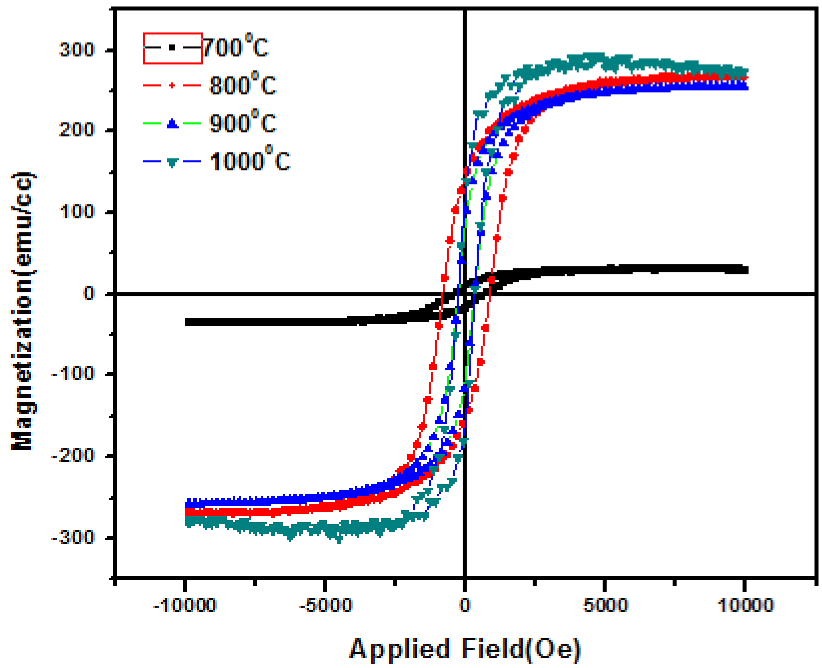


Fig.4.4*M-H*loops for cobalt ferrite films annealed at different temperatures.

Table: 4.3 Magnetic properties of cobalt ferrite thin film at different temperatures.

T **(°C)**	**M_s (emu/g)**	**M_r (emu/g)**	**H_c Oe**
700	32.3	12.4	545.4
800	264.6	150.4	841.6
900	252.9	101.3	287.5
1000	284.6	137.9	293.5

Fig. 4.5 shows the variationofM_s, $M_r$and $H_c$with temperature.

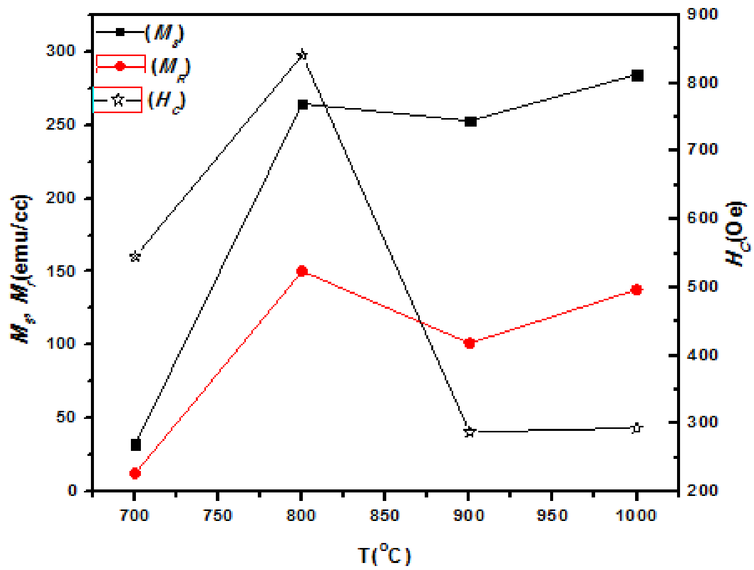


Fig. 4.5 Temperature verses M_S, M_r and H_C

To further understand the effect of thickness on the magnetic properties, films of different thickness has been deposited and annealed 800°C and 900°C. Fig. 4.6 (a, b) shows the *M-H* loops of cobalt ferrite film with different thickness annealed at 800°C and 900°C.It is clear from the figure that thickness has no significant effect on the M_s and H_c. The M_s is structure insensitive property, therefore any change in the thickness will not affect it. However, coercivity depends upon the grain size as well as particle size, which is well evident from the films annealed at different temperature. The film annealed at 900°C has low coercivity as compared 800°C. Since higher temperature promotes grain growth and reduces coercivity. Table 4.4 shows the magnetic properties of the films with different thickness.

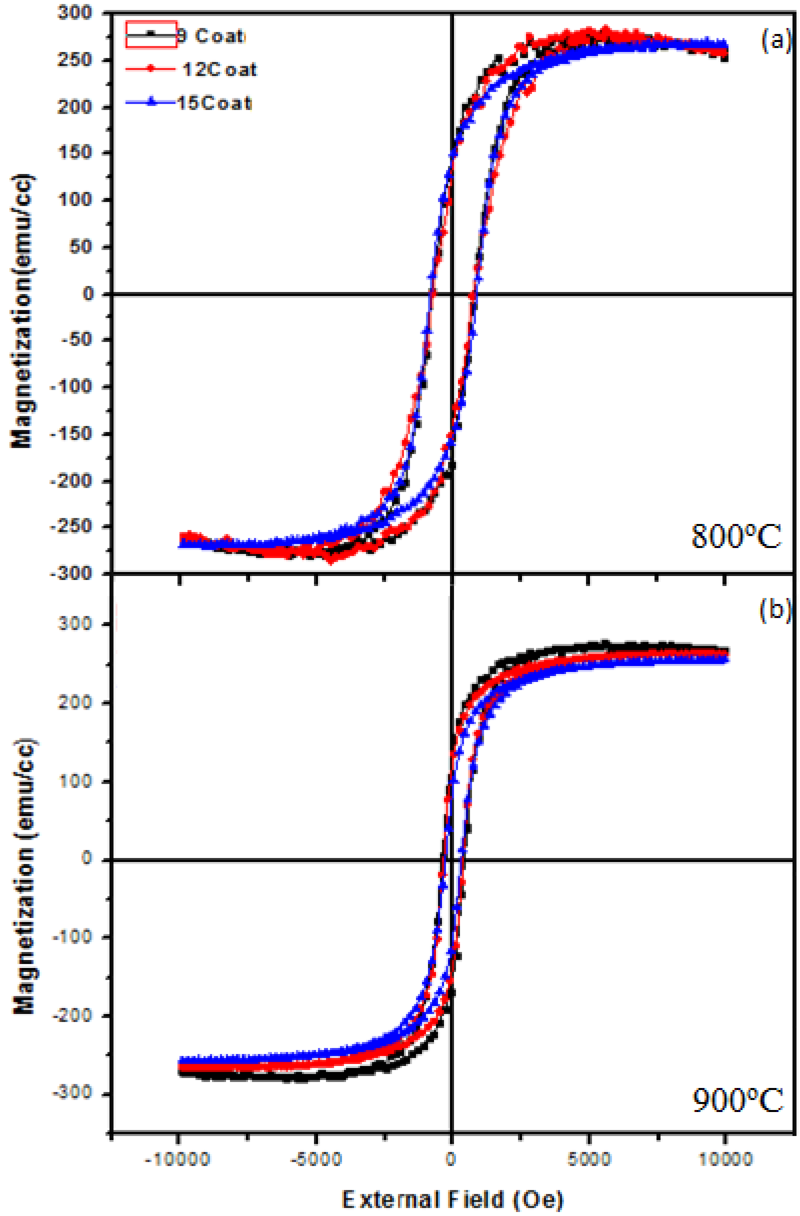


Fig. 4.6 (a,b)*M-H* loops for cobalt ferrite films annealed at 800°Cand 900°C with different thickness.

Table: 4.4 Magnetic properties of cobalt ferrite thin film annealed at 800°C and 900°C with different thickness.

T **(°C)**	**Thickness (nm)**	**M_s (emu/g)**	**M_r (emu/g)**	**H_c Oe**
800	414	259.8	158.5	767.6
	552	257.8	149.4	793.4
	691	266.7	143.5	841.6
900	414	268.6	150.6	400.5
	552	263.6	133.7	350.8
	691	256.4	96.2	287.5

4.3 Field Emission Scanning Electron Microscope

The surface morphology of cobalt ferrite thin films has been studied by using high resolution FE-SEM. Fig.4.7 shows the FE-SEM images of cobalt ferrite thin film deposited on alumina substrate heat treated at 900°C for 1 h. The well distinguished particles were observed on the film surface, which suggests that film were properly deposited.

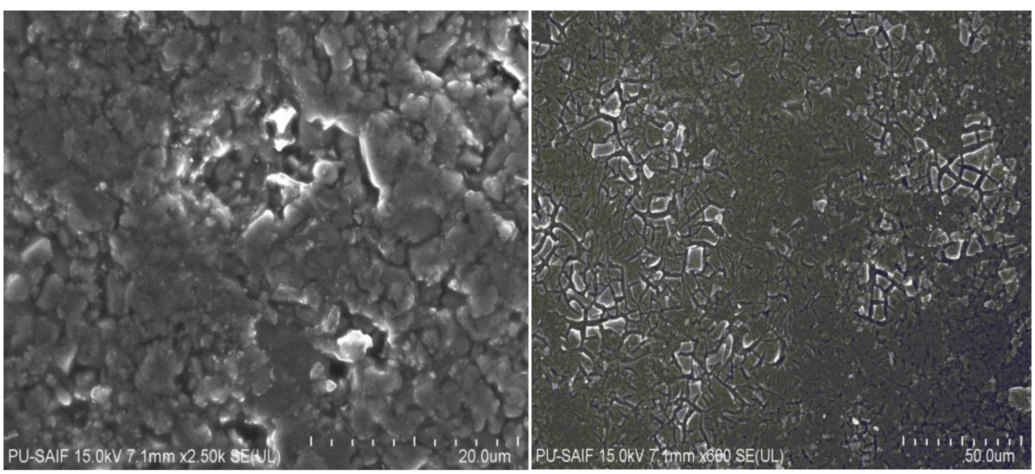


Fig. 4.7 FE-SEM images of cobalt ferrite thin films.

The cobalt ferrite powder and thin films (0.40-0.70µ thickness) have been successfully prepared by sol gel and spin coating method respectively on alumina (Al_2O_3) substrate. The effect of annealing temperature and film thickness on the structural and magnetic properties were investigated. Single phase cobalt ferrite was confirmed by X-ray diffraction pattern. The XRD peaks of cobalt ferrite film were not distinguished from substrate peaks due close diffraction angles. It was found the annealing has significant effect of magnetic properties. M_s found to increase with increasing annealing temperature and found maximum 284.6emu/cc for the films annealed at 1000^{o}C. A well saturated soft magnetic *M-H* loop were observed for films and powder.

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