CHAPTER: 3

EXPERIMENTAL TECHNIQUES

3.1 Introduction:

Characterization of the prepared material is an important step. A wide variety of characterization techniques were used to evaluate the material quality of the thin films before using the films in applications. The thickness of the film is measured using surface profiler. The structural properties of the films were studied by X-ray diffraction (XRD) technique, scanning electron microscopy (SEM). The RMS roughness of the films was studied by atomic force microscopy (AFM). The magnetic properties were studied by using vibrating sample magnetometer (VSM). The electrical property was studied by D.C. two point probe method. Dielectric properties were measured by using with LCR Meter Bridge. The water contact angle against water was measured using a contact angle meter. The optical properties were studied by spectrophotometer.

In this work, the different experimental techniques used for the characterization and measurement of various properties of the cobalt and nickel ferrite thin films were discussed.
3.2 X-ray diffraction technique:

X-Ray Diffraction (XRD) is a powerful technique used to uniquely identify the crystalline phases present in materials in bulk and thin form and to measure the structural properties (strain, grain size, epitaxy, phase composition, preferred orientation, and defect structure) of these phases.

XRD offers unparalleled accuracy in the measurement of the atomic spacing and is the technique of choice for determining strain state in thin films. XRD is noncontact and nondestructive, which make it ideal for situ studies. The intensities measured with XRD can provide quantitative, accurate information on the atomic arrangements at interface (e.g. multilayers).

Materials composed of any element can be successfully studied with XRD, but XRD is most sensitive to high-Z elements, since the diffracted intensity from these is much larger than from low-Z elements. As a consequence, the sensitivity of XRD depends on the material of interest. With lab-based equipment, surface sensitivities down to a thickness of 50 Angstrom are achievable, but synchrotron radiation (because of its intensity) allow the characterization of much thinner films, and for many materials, monatomic layers can be analyzed.
While XRD is nondestructive and can be used in most environments, TEM and electron diffraction are destructive and require high vacuum. One of the disadvantages of XRD, compared to electron diffraction, is the low intensity of diffracted X-rays, particularly for low-Z materials. Typical intensities for electron diffraction are $\sim 10^8$ times larger than for XRD. Because of the small diffracted intensities, thin-film XRD generally require large specimens ($\sim 0.5$ cm) and the information acquired is an average over a large area. XRD does not provide spatial resolution, but for special applications, resolution greater than $\sim 10$ $\mu$m can be obtained with micro focus source and a suitably thick film ($\sim 1$ $\mu$m). The use of intense synchrotron X-ray radiation mitigates these two disadvantages somewhat; however, the XRD analysis of thin films with synchrotron radiation is not routine.

Thin film is important in many technological applications, because of its ability to accurately determine strains and to uniquely identify the presence and composition of phases. In semiconductor and optical materials applications, XRD is used to measure the strain state, orientation and defects in epitaxial thin films, which affect the film’s electronic and optical properties. For magnetic thin films, it is used to identify phases and to determine preferred orientations, since
these can determine magnetic properties. In metallurgical applications, it is used to determine strains in surface layers and thin films, which influence their mechanical properties. For packaging materials, XRD can be used to investigate diffusion and phase formation at interfaces.

**The fundamental principle of XRD:**

![Figure 3.1 Basic features of XRD experiment.](image)

![Figure 3.2 Millar indices of atomic planes in a simple cubic crystal.](image)

Figure 3.1 and 3.2 shows the basic features of an XRD experiment, where the diffraction angle $2\theta$ is the angle between the incident and diffracted X-rays. In typical experiment, the diffracted intensity is
measured as a function of $2\theta$ and orientation of the specimen, which yields the diffraction pattern [1-3].

**X-ray diffraction using X-ray two probe crystal structure**

X-rays are the electromagnetic radiations of very short wavelength of the order of 1 Å. When the electron jumps from higher energy level to lower energy level to fill up the created vacancies, X-rays are emitted.

**The direction of diffracted X-rays**

Crystals consists of planes of atoms that are spaced a distance $d$ apart, but can be resolved into many atomic planes, each with a different $d$-spacing. Any atomic plane can be uniquely distinguished by Miller indices. The $d$-spacing between $(hkl)$ planes is denoted by $d_{hkl}$ and for cubic crystals, it is represented by an equation.

$$d_{hkl} = \frac{a_0}{\sqrt{h^2+k^2+l^2}}$$  \hspace{1cm} 3.1

where $a_0$ is a lattice constant of the crystal.

When there is constructive interference from X-ray scattered by the atomic planes in the crystal, a diffraction peak is observed. The condition for constructive interference from plane with spacing $d_{hkl}$ is given by Bragg’s law.

$$\lambda = 2d_{hkl} \sin \theta_{hkl}$$  \hspace{1cm} 3.2
where $\theta_{hkl}$ is the angle between the atomic planes and incident X-ray beam [4]. Scherrer [5] equation is used to determine crystallite size of thin film.

$$D = 0.9 \frac{\lambda}{\beta \cos \theta}$$  

3.3 Scanning Electron Microscopy:

The SEM is the most widely used instrument for obtaining topographical features of a film. The SEM was first developed by Von Advenne [6] and is used to determine grain size, porosity and grain boundary. A finely focused electron beam is scanned over the surface of the specimen and the secondary electrons emanating from the specimen are used for the Z-modulation in a corresponding raster on a TV or oscilloscope screen. Frequently, a thin layer of gold is deposited on the specimen surface (without altering the surface features) to avoid charging problems. For topographical feature determination, the secondary electron mode is generally preferred since these electrons emanate only form about 10 Å or less from the film surface and hence the picture obtained is a faithful reproduction of the surface features. The schematic diagram of Scanning Electron Microscopy (SEM) is shown in Fig. 3.3.
The SEM is an intermediate between the optical microscope and the TEM. The magnification that can be obtained is \(~3\) to \(10^5\). The resolution is \(~30\ \text{Å}\) and a depth of focus, a few hundred times that of a light microscope [7]. Quantitative topography can be done by taking two photographs of the same area at two tilt angles, usually differing by 6-10°. The stereo-pair that is thus obtained is then viewed in a stereomicroscope. Fractured thin films can also be seen along the cross-section for obtaining additional information e.g. thickness of the film, grain size, columnar structure etc.
The SEM has several modes of operation which is decided by the nature of the excited particles that are analyzed when the electron beam is striking the specimen. The backscattered (elastically scattered) electron picture also gives some information about the surface microstructure in addition to a weak atomic number contrast.

3.4 Vibrating Sample magnetometer.

A vibrating sample magnetometer (VSM) operates on Faraday’s law of induction, which tells us that a changing magnetic field will produce an electric field can be measured and can tell us information about the changing magnetic field. When a material is placed in a uniform magnetic field, a dipole moment gets induced in the sample proportional to the product of the sample susceptibility and the applied field, if the sample is made to undergo sinusoidal motion, the resulting magnetic flux changes near the sample will induce an electric signal in suitable placed stationary coils. The signal is proportional to the moment, amplitude, and frequency of vibration.

The sample in thin film form were kept in cylindrical tubes (1mm diameter and 2mm long) carefully. One end of the tube is already closed and the other end was closed by cotton after filling the sample. The weight of empty tube and weight of the tube with sample
were measured so as to get the weight of the sample taken for the experiment. These tubes were loaded in between the electromagnet using a long sample holder.

![Schematic diagram of VSM](image.png)

Fig. 3.4 schematic diagram of VSM

The sample holder is mounted on electromechanical transducer, which passes through the center of driving coil. The transducer is driven by a power amplifier which itself is driven by an
oscillator, the sample under study is constraint to vibrate only along the vertical axis. When the sample vibrates vertically, it induces a signal in the pickup coil. The pail of stationary coils picks up the induced ac signal. The output of the sample coil is fed to the differential input of a lock in amplifier. The reference input of the lock in amplifier comes from the sine wave oscillator used to drive the sample holder. The output of the lock in amplifier as well as the strength of the applied field measured by gauss meter whose probe is placed at the center of electromagnet given to data acquisition system. The schematic diagram of VSM is shown in Fig. 3.4.

3.5 Atomic Force Microscope

The Atomic Force Microscope (AFM) is being used to solve processing and materials problems in a wide range of technologies affecting the electronics, telecommunications, biological, chemical, automotive, aerospace, and energy industries. The materials being investigating include thin and thick film coatings, ceramics, composites, glasses, synthetic and biological membranes, metals, polymers, and semiconductors. The AFM is being applied to studies of phenomena such as abrasion, adhesion, cleaning, corrosion, etching, friction, lubrication, plating, and polishing. By using AFM one can not
only image the surface in atomic resolution but also measure the force at nano-newton scale [8]. The publications related to the AFM are growing speedily since its birth.

The first AFM was made by meticulously gluing a tiny shard of diamond onto one end of a tiny strip of gold foil. In the fall of 1985 Gerd Binnig and Christoph Gerber used the cantilever to examine insulating surfaces. A small hook at the end of the cantilever was pressed against the surface while the sample was scanned beneath the tip. The force between tip and sample was measured by tracking the deflection of the cantilever. This was done by monitoring the tunneling current to a second tip positioned above the cantilever. They could delineate lateral features as small as 300 Å. The force microscope emerged in this way. In fact, without the breakthrough in tip manufacture, the AFM probably would have remained a curiosity in many research groups. It was Albrecht, a fresh graduate student, who fabricated the first silicon microcantilever and measured the atomic structure of boron nitride. Today the tip-cantilever assembly typically is microfabricated from Si or Si$_3$N$_4$. The era of AFM came finally when the Zurich group released the image of a silicon (111) 7X7 pattern. The world of surface science knew that a new tool for surface microscope was at hand. After several years the microcantilevers have
been perfected, and the instrument has been embraced by scientists and technologists. Fig. 3.5 shows line diagram of a typical Atomic Force microscope (AFM).

![Line diagram of a typical Atomic Force microscope.](image)

The force between the tip and the sample surface is very small, usually less than $10^{-9}$ N. How to monitor such a small force is another story. The detection system does not measure force directly. It senses the deflection of the microcantilever. The detecting systems for monitoring the deflection fall into several categories. The first device introduced by Binnig was a tunneling tip placed above the metallized surface of the cantilever. This is a sensitive system where a change in spacing of 1 Å between tip and cantilever changes the tunneling current by an order of magnitude. It is straightforward to measure deflections smaller than 0.01 Å. Subsequent systems were based on the optical techniques. The interferometer is the most sensitive of the optical methods, but it is somewhat more complicated than the
beam-bounce method which was introduced by Meyer and Amer. The beam-bounce method is now widely used as a result of the excellent work by Alexander and colleagues. In this system an optical beam is reflected from the mirrored surface on the back side of the cantilever onto a position-sensitive photodetector. In this arrangement a small deflection of the cantilever will tilt the reflected beam and change the position of beam on the photodetector. A third optical system introduced by Sarid uses the cantilever as one of the mirrors in the cavity of a diode laser. Motion of the cantilever has a strong effect on the laser output, and this is exploited as a motion detector. The front view of scanning probe microscope is shown in figure 3.6

![An AFM scanning head from Digital Instruments.](image)

**Fig. 3.6 Photographic front view of scanning probe microscope**
3.6 UV-Visible spectroscopy:

UV-Vis Absorption spectroscopy measures the percentage of radiation that is absorbed at each wavelength. Typically this is done by scanning the wavelength range and recording the absorbance. UV-Vis absorption spectroscopy is widely used in organic chemistry to investigate the extent of multiple bond or aromatic conjugation within molecules. Frequently, organic chemists have used liquid solutions, because solvents such as ethanol and hexane do not absorb in the UV-Vis range and solutions can be easily prepared for many organic compounds. The technique can be expanded to gases and solids, and also beyond absorption to include measuring reflected rather than transmitted light.

UV-Vis spectra tend to be broad in nature due to the fact that vibrational and rotational levels of the molecular orbitals are superimposed upon the electronic levels. This produces a combination of overlapping lines that appear as a continuous absorption band in the UV-Vis spectrum.

Measurement of the optical band gap of thin films:

A classical semiconductor exhibits minimal optical absorption for photons with energies smaller than the band gap and high absorption for photons with energies greater than the bandgap. As a
result, there is a sharp increase in absorption at energies close to the band gap that manifests itself as an absorption edge (or “reflection threshold”) in the UV-Vis absorbance spectrum.

The optical absorbance of thin film was studied using UV-VIS spectrophotometer in the wavelength range of 350-900 nm, which has been further used for the calculation of band gap energy. The data were analyzed from the following classical relation for near edge optical absorption in semiconductors which gives the relation between the optical band gap, absorption coefficient and energy (hv) of the incident photon [9].

\[
\alpha = \frac{[A(h\nu - E_g)^{n/2}]/h\nu}{3.4}
\]

where A is a parameter, independent of hv [10] and \(E_g\) the optical band gap energy, \(n\) a number equal to one for direct gap and four for indirect gap compounds. Plotting the dependence of \((\alpha h\nu)^2\) and \((\alpha h\nu)^{1/2}\) on \(h\nu\), the values of direct and indirect band gap can be determined by extrapolating the linear portions of these plots to \((\alpha h\nu)^2\) equal to zero and \((\alpha h\nu)^{1/2}\) equal to zero respectively.

3.7 Water contact angle measuring methods:

The contact angle is the angle at which a liquid/vapor interface meets a solid surface. The contact angle is specific for any given
system and is determined by the interactions across the three interfaces. Most often the concept is illustrated with a small liquid droplet resting on a flat horizontal solid surface. The shape of the droplet is determined by the Young's relation. The contact angle plays the role of a boundary condition. Contact angle is measured using a contact angle goniometer. The contact angle is not limited to a liquid/vapour interface; it is equally applicable to the interface of two liquids or two vapours. The use of Contact Angle in characterizing the quality of a surface treatment is by far the most accurate and repeatable method available in the industry today. Contact angle measurement enables different types of surface treatments to be compared to one another, with the generated data accurately correlating to measures of adhesion, material wettability, biocompatibility, and lubricity.

Fig.3.7 Image of water drop on glass from contact angle device.
3.7.1 Typical contact angles:

Consider a liquid drop on a solid surface. If the liquid is very strongly attracted to the solid surface (for example water on a strongly hydrophilic solid) the droplet will completely spread out on the solid surface and the contact angle will be close to 0°. Less strongly hydrophilic solids will have a contact angle up to 90°. On many highly hydrophilic surfaces, water droplets will exhibit contact angles of 0° to 30°. If the solid surface is hydrophobic, the contact angle will be larger than 90°. On highly hydrophobic surfaces the surfaces have water contact angles as high as ~120° on low energy materials e.g. fluorinated surfaces. However some materials with highly rough surface may have water contact angle greater than 150°. These are called superhydrophobic surfaces. Sometimes the contact angle is measured through the gas instead of through the liquid, which reverses 0 and 180 in the above explanation [11,12]. Fig.3.7 shows image of water drop on glass from contact angle device.

3.7.2 Thermodynamics:

The theoretical description of contact arises from the consideration of a thermodynamic equilibrium between the three phases: the liquid phase of the droplet (L), the solid phase of the substrate (S), and the gas/vapor phase of the ambient (V) (which will
be a mixture of ambient atmosphere and an equilibrium concentration of the liquid vapor). The V phase could also be another (immiscible) liquid phase. At equilibrium, the chemical potential in the three phases should be equal. It is convenient to frame the discussion in terms of the interfacial energies. We denote the solid-vapor interfacial energy (see surface energy) as $\gamma_{SV}$, the solid-liquid interfacial energy as $\gamma_{SL}$ and the liquid-vapor energy (i.e. the surface tension) as simply $\gamma$, we can write an equation that must be satisfied in equilibrium (known as the Young Equation):

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos(\theta_C)$$  

Where $\theta_C$ is the equilibrium contact angle. The Young equation assumes a perfectly flat surface, and in many cases surface roughness and impurities cause a deviation in the equilibrium contact angle from the contact angle predicted by Young's equation.

An FTS technology offers the surface treatment industry a compact camera based Contact Angle Instrument for measuring the contact angles of liquids on solids and Free Surface Energy of solids. The devices FireWire interface to a PC makes the instrument extremely fast, yet easy to install. The powerful droplet analysis software makes the measurements user independent and error free ensuring reproducible results. The instrument is accurate, simple, and
easy to use, yet extremely powerful. Designed for industrial, QC, education and R&D applications this Contact Angle Meter sets a new standard in surface treatment measuring technology.

![Goniometer](image.jpg)

Fig. 3.8 A photograph of Goniometer.

A contact angle goniometer shown in figure 3.8 is used to measure the contact angle.

3.8 Dielectric Studies:

The dielectric properties of ferrites basically depend on several factors such as chemical composition, method of preparation, grain structure, additives etc. These properties are sensitive to microstructure, grain size, grain boundaries and porosity. The study of frequency depends of dielectric behavior gives valuable information regarding localized charge carriers and dielectric polarization. There are various possible mechanisms for polarization in dielectric material. One process is common to all the materials, in electronic polarization that is the shift of center of negative electron cloud in relation to the
nucleus. The second mechanism is displacement of the positive and negative ions in relation to one another, called the ionic polarization. The rest are orientation and space charge polarization. In ferrites the possible mechanism for polarization are electronic, ionic and space charge.

The dielectric constant and loss was studied as a function of frequency in the range from 100 Hz to 1MHZ at room temperature were carried out using a LCR-Q meter bridge (HPLCR 4284A). The electrodes of sample were painted with silver paste to ensure good electric contacts. The dielectric constant ($\varepsilon'$) was calculated by the formula,

$$\varepsilon' = \frac{C}{\varepsilon_0 A}$$  \hspace{1cm} 3.6

Where, $C$ is capacitance in Farad, $d$ is thickness of the film in meter, $A$ is area of upper contact and $\varepsilon_0$ is a constant called permittivity of free space in SI unit its value is $8.85 \times 10^{-12}$.

The dielectric loss factor has been calculated from the relation:

$$\varepsilon'' = \varepsilon' \tan \delta$$  \hspace{1cm} 3.7

Where, $\tan \delta$ is the tangent loss [13].
3.9 Electrical Resistivity Measurement:

Investigation of critical resistivity as a highly structure sensitive properties make it possible to be an insight into the structural and electrical properties of the metal films which is important from both the theoretical and practical point of view.

The contact methods are most widely used for the measurement of resistivity; these methods include two-point probe, four point probe and the spreading resistance. The two-point probe method is simple, easy to use and useful for high resistive thin films. The experimental set up for the measurement of d. c. resistivity of thin film is shown in fig. 3.9. In this method, constant voltage ‘V’ is applied between two-fixed positions probes separation ‘d’ and current passing thorough a sample of known dimensions (cross section area A) is measured with an appropriate current meter. For uniform sample the resistivity is given by,

$$\rho = \frac{A}{l} \times \frac{V}{d}$$  \hspace{1cm} 3.8

In case of semiconducting thin films, resistivity decreases with increase in temperature. The thermal activation energy ‘Ea’ are calculated by using resistivity.

$$\rho = \rho_0 \exp\left(\frac{-Ea}{k.T}\right)$$  \hspace{1cm} 3.9
Where, symbols have their usual meanings. The slope of \( \log \rho \) versus \((1000/T)\) leads to the estimation of activation energy. The resistivity measurement of material gives information of room temperature resistivity, activation energy, and type of material (NTC or PTC). However, there is disadvantage of metal contact, which forms a low resistance ohmic or non-ohmic junction with material. The metal contacts forms heating effect of current, especially when sample resistivity is high [14].

Fig. 3.9 D.C. two probe set up for the measurement of d. c. resistivity of thin film.

3.10 LPG Gas sensing application:

The evolution of gas sensors are closely parallel developments in microelectronics, in that the architecture of sensing elements is influenced by design trends in planer electronics, and one of major
goals of the field is to design nano-sensors that could be easily integrated with modern electronic fabrication methods. Many of semiconducting metal oxides have been found to be good candidates for gas sensing since they exhibit significant variations of the electrical resistance on contact with ambient gases and vapors. The ideal sensing material for gas sensor should have low cost, small size, maintenance free and long durability. The performance of gas sensor changes with the nature of sensing material [15,16].

Nanostructures in the form of thin films, nanoparticles, nanoporous materials, nanocomposites, and bulk nanocrystalline materials are of interest both for basic scientific research and technological applications as their properties are dominated by the extremely large specific surface areas. Such surfaces have generally unique properties which greatly differ from those of bulk materials, and which may even acquire characteristic size dependence at the nanometer scale. Because of the high surface-to-volume ratio, local phenomena, such as adsorption or changes in the surface electronic state, may contribute significantly to the overall properties of the materials.

The sensor performance is strongly dependent on the microstructural features such as crystallite size, grain boundary characteristics and thermal stability [17]. Therefore, one can improve
the sensitivity by controlling the grain size and surface morphology. The effect of the different surface treatments on active sensor surface will certainly cause the change in morphological properties of sensing material and hence on the sensor performance [18-19].

As we know, that the surface morphology and the grain size dependent on the preparation method. The present work investigates the effect of ferrite thin films on magnitude and performance of gas response, prepared by spray pyrolysis method.

A dc two-point probe measurement technique was used to measure the electrical resistance in the presence of LPG gas and air atmosphere. For electrical measurements, silver paste contacts of 1 mm were applied at the edges of the ferrite thin films separated by 1 cm, as top electrodes whose Ohmic nature was tested within ± 10 V. The electrical resistance of ferrite thin film in air (Ra) and in gas atmosphere (Rg) was measured to evaluate the gas sensitivity defined as follows

\[
\text{Sensitivity } S (\%) = \frac{R_a - R_g}{R_a} \times 100
\]

where, \( R_a \) is the stabilized resistance of cadmium oxide in air atmosphere and \( R_g \) is the resistance in the presence of target gas.
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