Chapter 2

Synthesis and Characterization of Materials
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2.1 Introduction:

In the field of condensed matter physics and materials science the first and important step during the experimental research is synthesis of materials and selection of synthesis parameter such like temperature, pressure and time for reaction. The quality of bulk as well as thin film depends on the synthesis method used. Furthermore, the proper selection of synthesis parameters helps to achieve desired properties. The selection of synthesis parameters depends on the sample requirement. The use of high purity starting materials helps to avoid the introduction of defects into the structure.

Various synthesis methods such as cost effective Sol-gel route and conventional solid state reaction method for polycrystalline bulk and chemical solution deposition (CSD), and pulse laser deposition (PLD) for thin film are available for the synthesis of single crystalline manganite thin films. In CSD technique, we have used sol-gel technique in which the mixing, stirring and heating of appropriate stoichiometric quantities of the metal acetates in a distilled water and acetic acid resulted in a clear solution of the constituents used for deposition. In CSD method, the parameters such as temperature and annealing time were varied to achieve desired physical properties. In the PLD technique, dense and single-phase bulk target is used for the ablation process to make good quality films. Therefore, the selection of sample preparation method is a crucial factor. The synthesis of polycrystalline bulk target samples is broadly divided into two categories namely; 1) solid state reaction method and 2) chemical route comprising sol-gel technique, nitrate route, co-precipitation technique, etc. [1-3]. Due to its simplicity, all the bulk polycrystalline samples studied during the course of present work have been synthesized using the solid-state reaction method. In order to prepare a single-phase sample, the synthesis conditions during any reaction are very important. During synthesis, the parameters such as temperature, pressure, gas flow and time for the reaction are needed to be varied according to phase requirements in the sample. Mapping of all variables has to be made to select the conditions, which are best suited for each material and phase.
2.2 Synthesis Methods:

2.2.1 Chemical Solution Deposition Technique:

Advanced chemical liquid phase synthesis methods consisting of novel co-precipitation and sol-gel processing involves the simultaneous occurrence of nucleation, growth, coarsening and/or agglomeration processes and is the most preferable alternative for the preparation of oxide nanomaterials and thin films. The method offers high degree of homogenization together with the small particle size and thereby speeds up the reaction rate and much lower reaction temperature are sufficient for the reaction to occur. Further, chemical route is relatively simple, cost effective and requires only low synthesis temperature as compared to vacuum deposition techniques. The precipitation of oxides from both aqueous and non-aqueous solutions can generally be broken into two categories: those which produce an oxide directly and those which produce what is best termed a precursor that must be subjected to further processing (drying, calcination, etc.).

In either case, mono-dispersed nanoparticles of oxides, like those of metals, frequently require a capping ligand or other surface bound stabilizer to prevent agglomeration of the particles. In the cases where calcination or annealing of the samples is necessary, some agglomeration will be unavoidable. The products of co-precipitation reactions, particularly those performed at or near room temperature are usually amorphous. It is extremely difficult to experimentally determine whether the
as-prepared precursor is a single phasesolid solution or a multiphase, nearly-homogeneous mixture of the constituent metal hydroxides, carbonates and/or oxides that react to form a single phase mixed metal oxide when heated.

Figure 2.1: Flow Chart of the Chemical solution deposition technique
2.2.2 Spin coating method:

Chemical Solution Deposition (CSD) using a spin coater is another effective technique to obtain the polycrystalline and single crystal thin films and is highly inexpensive technique as compared to PLD and sputtering methods. By using, CSD method, epitaxial and polycrystalline thin films can be deposited through many routes. The synthesis of the manganite thin films was carried out by dissolving the stoichiometric amounts of metal acetates such as Yttrium Acetate \([\text{Y (CH}_3\text{CO}_2\text{)}_3 \times \text{XH}_2\text{O}],\) Calcium Acetate \([\text{Ca (CH}_3\text{CO}_2\text{)}_2 \times 4\text{H}_2\text{O}]\) and Manganese Acetate \([\text{Mn (CH}_3\text{CO}_2\text{)}_2 \times 4\text{H}_2\text{O}]\) in acetic acid and distilled water. This precursor solution was then heated \((80 \, ^\circ\text{C})\) and stirred until the clear aqueous solution formed which was used for the thin film deposition. Thin films were then heated at \(350^\circ\text{C}\) and annealed at different temperatures varying from \(700^\circ\text{C}\) and \(900^\circ\text{C}\). The CSD method helps in controlling the particle size by varying the RPM (rotations per minute) of the spin coater. The deposited thin films sintered at different temperatures decide the connectivity and compactness of the thin films. The deposition parameters can be optimized to obtain physical properties of the thin films exhibiting large magnetoresistance in low fields and near room temperature.

![Flow Chart of the Spin Coater technique used in preparation of Thin film](image)

**Figure 2.2:** Flow Chart of the Spin Coater technique used in preparation of Thin film
2.2.3 Dip Coating Method:

Dip coating is simple and one of the oldest coating methods. Dip-coating process includes five stages: immersion, start-up, deposition, evaporation and drainage. In the dip-coating method, the substrate is slowly dipped into and withdrawn from a tank containing the sol, with a uniform velocity, in order to obtain a uniform coating. A microprocessor based system along with user friendly software takes care of accurate control throughout the process. Speed, traverse and idling duration can be programmed through the computer. Dip coating is done by immersing a substrate into a tank containing the coating material, removing from the tank, and allowing it to drain. The coated piece can then be dried by force-drying or baking. Film formation in dipping is dependent on the viscosity of the fluid. The viscosity of the fluid in a dip tank must remain practically constant if the deposited film quality is to remain high. Dip coating is well suited for high production coating of relatively simple shapes. Transfer efficiency is very high, all contact areas are coated, equipment requirements are low, and the process can be automated.

![Dip Coating Diagram](image)

**Figure 2.3**: A schematic diagram of Dip coating technique

2.2.4 Spray Pyrolysis Technique:

This coating technique was the predecessor of the chemical vapor deposition (CVD) techniques. The coating is applied at elevated temperatures by spraying
droplets of liquid precursors onto hot substrates. The major advantages of spray pyrolysis are that the coatings are more durable than vacuum deposited coatings, the variety of precursors could be used, and the process can be employed at lower cost than CVD or vacuum deposition. The disadvantage is that the coatings are not uniform in thickness. CVD consists of vaporizing the precursors and directing the resultant gases onto a hot substrate.

In spray pyrolysis the precursor solution is pulverized as a fine mist via a spray nozzle and a carrier gas at high pressure. The so produced mist condenses on a preheated substrate, and is instantly pyrolysis (spray pyrolysis). The process can be conducted in one or more pulses to obtain uniform films. Spray pyrolysis is suitable for substrates with complex geometry, and can be used for a variety of oxide materials. The set-up used is illustrated below. It comprises a spray nozzle, a rotating heating plate and a container. The whole is mounted in a protective chamber which can be filled with protective or reactive gases. The nozzle is driven pneumatically via a computer controlled control unit.

The advantages of spray pyrolysis are summarized below:

- the spray pyrolysis can be easy and cheap
- Substrates with complex geometries can be coated
- Leads to uniform and high quality coating
- Low crystallization temperature
- Porosity can be easily tailored
2.2.5 Ceramic Method:

The most common method of synthesizing inorganic solids is by the reaction of the component materials at elevated temperatures. If all the components are solids the method is called the ceramic method. As the name suggests, the solid form of the constituents are reacted at high temperatures for a certain minimum period of time which is generally attained by resistance heating. The general procedure involved in solid-state reaction method for producing mixed valent manganite oxides is described below.

The stoichiometric composition of constituent materials in the form of carbonates, oxides, etc. (all 99.99% pure Aldrich make) were preheated for appropriate time and temperature (350°C to 550°C) to remove the low temperature volatile impurities and then weighed in proportionate quantities according to the desired composition. In the solid state reaction, for the reaction to take place homogeneously, it is very important to mix and grind the powders thoroughly for long duration to obtain homogeneous distribution in required proportions of the desired stoichiometric compound. The proper grinding of mixed powders using pestle-mortar

Figure 2.4: Spray pyrolysis set up
decreases the particle size, which is necessary for obtaining close contact among the atoms so that the right material is formed. This powdered mixture was then heated in air at about 950°C. During the first calcination, CO₂ is liberated from the mixture. After successive calcinations, the compounds were reground, palletized and sintered for a long time (~100 hours) in the temperature range 1100°C - 1350°C. Before every sintering of samples, the samples were ground thoroughly to obtain back powders until the particle size reduced to ~ 40 micron size by using suitable sieves and then pressed into cylindrical pallets. Many intermediate grindings are required to get appropriate phase formation and phase purity. These heating in atmospheric conditions are required to obtain single phasic material and to release the remaining CO₂, if any. The final sintering was carried out at a sufficiently high temperature (in the range 1350-1400°C) to get the better crystallization. The furnace was turned off and the samples were left inside to cool to RT.

The solid-state reaction method has proved to be the most suitable for synthesizing reproducible samples of manganite oxides.
Figure 2.5: Flow Chart of the sample preparation method used

Synthesis and Characterization of Materials
2.2.6 Laser ablation Technique:

The interest in the use of pulsed Laser Deposition (PLD) technique for the thin film synthesis is mainly due to the good quality of films of mixed oxide materials prepared using this technique as compared to other methods. This technique is also used to deposit the thin films of multi component oxides such as ferroelectric and ferrites [9, 10]. The ease, with which oxide ceramic materials can be grown as high quality thin films using PLD method, makes it as important technique for the growth of oxide thin films.

**Figure 2.6:** A schematic illustration of a typical pulsed laser deposition (PLD) system.

A schematic illustration of a typical PLD system is as shown in figure: 2.6. Usually, excimer laser is used for deposition. Between the output port of the laser and the port of the deposition chamber, optical elements are placed in order to steer and focus the laser beam. The optical elements that couples the energy from the laser to the target are lenses and apertures, such as mirrors, beam splitters, and laser windows.
Once the laser beam passes through the optical elements it enters the deposition system and is focused onto the surface of the target. All the elements in the target are then rapidly heated up to their evaporation temperature. The emitted materials tend to move towards the substrate, and condense on the substrate. Well-polished substrate located at a typical distance from the target is stationary or rotated for homogenization of the deposited material. The temperature of the substrate may be kept between RT and 850°C. This temperature depends upon the nature of material used for ablation. A gas supply is often provided to produce desired chemical reaction during film growth. Mixed oxide materials are prone to lose oxygen during the deposition. Therefore, during deposition of such oxide materials, certain optimum partial pressure of oxygen is maintained during the deposition. During the course of present work, the O₂ partial pressure was maintained at 400 mTorr. The vacuum chamber is made up of stainless steel and is evacuated down to 10⁻⁶ bar by using a turbo pump.

The most important feature of PLD is that, the stoichiometry of the target can be retained in the deposited films. This is the result of the extremely high heating rate of the target surface (≈10⁸K/s) due to pulsed laser irradiation. It leads to the congruent evaporation of the target regardless of the vaporizing temperature of the constituent elements of compounds of the target.

2.2.7 Principle of PLD:

The principle of pulsed laser deposition is a very complex physical phenomenon. It comprises many processes in a chain namely, 1) the physical process of the laser-material interaction on solid target followed by 2) the formation of plasma plume with high energetic species and 3) the transfer of the ablated material through the plasma plume onto the heated substrate surface. Firstly, the pulsed laser beam is focused onto the surface of the target. This laser beam strikes the surface of the target material with sufficiently high energy and short pulse duration, which results into the rapid heating of the target elements up to their evaporation temperatures. Because of such a high energy, the elements are dissociated from the target surface and ablated out with stoichiometry as in the target. In most materials, the ultraviolet radiation is absorbed by only the outermost layers of the target up to a depth of ~ 1000 Å. The extremely short laser pulses (<50 ns) rapidly increase temperature of the surface to
thousands of degrees Celsius, but the bottom of the target remains virtually unheated. Such un-equilibrium heating produces a flash of evaporated elements that deposit on the substrate, producing a film with composition identical to that of the target surface. Rapid deposition of the energetic ablation species helps to raise the substrate surface temperature. In this respect PLD tends to demand a lower substrate temperature for crystalline film growth.

2.3 Structural and morphology Characterization:

The X-ray diffraction (XRD) technique used in analysis of crystal structures, finds a multitude of other applications in material science. Indeed much of our knowledge of the microscopic world has been derived from the persistent use of X-ray techniques. X-ray diffraction technique is highly useful in determination of phase purity of bulk polycrystalline material and epitaxy of the thin film. In the same way, surface morphological studies are of importance for the understanding of the films growth on the different substrate as well as grain size and surface roughness. Also surface morphology is highly useful to observe the defects created by the irradiation on the film surface, which has large impact on the physical properties and microstructure. During the course of work of this work, XRD measurements have been carried out on all the bulk targets and thin films to ascertain the structural purity and other important crystallographic information such as compressive and tensile strain and particle size.

Material surface morphology investigation is important to understand because the modifications in surface morphology cause the changes in many of the physical properties of material. To study surface morphology of materials numbers of the experiment techniques are available such as Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), Transmission electron microscopy (TEM) etc. The functional materials which are magnetic are interesting to study their magnetic surface morphology or magnetic behaviour at surface level which can be investigate by a variety of AFM is Magnetic Force Microscope (MFM). The MFM has a sharp magnetized tip which scans a magnetic sample; the tip-sample magnetic interactions are detected and used to reconstruct the magnetic structure of the sample surface.
2.3.1 X-ray diffraction (XRD) Studies:

X-rays are electromagnetic waves whose wavelength is in the neighborhood of 1Å. Except for the fact that their wavelength is so short, they have the same physical properties as other electromagnetic waves, such as optical waves. The wavelength of an X-ray is thus of the same order of magnitude as the lattice constants of crystals and it is this which makes X-rays useful in the analysis of crystal structures [11, 12].

![Diagram of X-ray diffraction](image)

**Figure 2.7:** Reflection of X-rays from a crystal. The reflected rays are nearly parallel because the detector is positioned far from the crystal. A smallest building block of unit cell

When a monochromatic X-ray beam is incident on the surface of a crystal, it is reflected. However, the reflection takes place only when the angle of incidence has certain values. These values depend on the wavelength and the lattice constants of the crystal, and consequently it seems reasonable to attempt to explain the selective
reflectivity in terms of interference effects, as in the physical optics. If we consider a crystal as a series of planes with their inter-atomic distance being ‘d’. Then the incoming X-ray, with wavelength, $\lambda$, will undergo scattering and interfere constructively only with that from adjacent planes at special angles ‘θ’, that satisfies the Braggs condition (Figure: 2.7)

$$n \cdot \lambda = 2dsin\theta$$

A crystal contains parallel planes along three different axes, so the actual measured values of θ vary with the alignment between the crystal planes and the incoming beam of X-rays. A plane perpendicular to the crystallographic a-axis is called the [100] plane; one perpendicular to b-axis is called [010] plane, and so on. Cell parameters $a$, $b$ and $c$ (length) and $\alpha, \beta, \gamma$ angles between $a$, $b$, and $c$ which can be determined by using XRD.

![Diagram](image.jpg)

**Figure 2.8:** Basic facts of typical XRD experimental setup used for the thin film

Figure 2.4 shows the schematic diagram of experimental setup for determination of the structure of thin films using XRD. Powder X-ray Diffraction (XRD) is the most widely used X-ray diffraction technique for characterizing polycrystalline materials [13]. From the XRD measurements, we can study the phase purity, crystallographic perfection, orientation relationship, and lattice constants of the manganite bulk and thin films.
Rietveld Analysis:

The Rietveld method refines a XRD data by comparing the observed diffraction pattern with the calculated from the known crystal structure. A least-square refinement is used to optimize the structure parameter [14,15].

The refinements of the XRD data of all the bulk samples studied were made using FULLPROF program. The order of refining the parameters was: the scale factor, the zero point for 2θ, five of the background parameters, the cell parameters, three of the peak shape parameters, the z co-ordinates, the isotropic displacement parameters, the occupation numbers, the fourth peak shape parameter, the anisotropic displacement parameters and the last background parameter. A few different routes to convergence were tried to confirm an optimal result. The R factors are good indicators if a route is not converging to a reliable result. Obtained cell parameters of bulk material are used to index the XRD peaks of the thin films.

Applications of XRD:

- XRD is nondestructive technique
- To identify crystalline phase and orientation
- To determine structural properties: Lattice parameters, strain, grain size, epitaxy, phase composition, preferred orientation (Laue) order-disorder transformation, thermal expansion
- To measure thickness of thin films and multi-layers
- To determine atomic arrangement

2.3.2 Scanning Electron Microscopy (SEM):

Various types of microscopes are available which can be divided into two groups (1) optical and (2) electron. With optical microscopes, particles down to a few micrometers (1μm= 10^4 Å=10^3 mm) in diameter may be seen under high magnification. The lower limit is reached when the particle size approaches the wavelength of visible light, 0.4 to 0.7μm for sub micrometer sized particles it is essential to use electron microscopy. Electron microscopy is an extremely versatile technique capable of providing structural information over a wide range magnification. At one extreme SEM compliments optical microscopy for studying the
texture, photography and surface features of powders or solid pieces, features up to
tens of micrometers in size can be seen. Because of the depth of focus of SEM
instruments, the resulting pictures have a definite three dimensional Quality.

SEM uses electrons as probes to form an image of the specimen. It is one of
the most powerful and productive methods of microscopy yet invented. The SEM has
allowed researchers to examine a large variety of specimens. SEM has many
advantages over traditional microscopes. It has a large depth of field, which allows
more specimens to be in focused at one time. The SEM also has much higher
resolution, so closely spaced specimens can be magnified at much higher levels. As
the SEM uses electromagnets rather than lenses, it is much more controlled in the
degree of magnification. All of these advantages, as well as the actual strikingly clear
images, make the scanning electron microscope one of the most useful instruments in
research today.

Scanning Electron Microscopy has become a valuable tool for examination
and evaluation of materials, both metallic and non-metallic, as well as assemblies and
surfaces. This is a non-destructive technique in a way that sample can be extracted as
such after scanning. The sample to be investigated is placed on a specimen stage
inside a vacuum enclosure of the SEM station and is incident with a finally focused
electron beam that can be static or swept in a cyclic fashion over the specimen’s
surface. The resulting signals that are produced when the scanning electron beam
impinges on the surface of the sample include both secondary emission electrons as
well as backscattered electrons. These signals vary as the result of differences in the
surface topography as the scanning electron beam is swept across the sample surface.

**Working of SEM:**

The SEM produces a largely magnified image by using electrons instead of
light to form an image. A beam of electrons is produced is produced at the top of the
microscope by an electron gun. The electron beam follows a vertical path through the
microscope, which is held within vacuum. The beam travels through electromagnetic
fields and lenses, which focus the beam down toward the sample. Once the beam hits
the sample, electrons and X-rays are ejected from the sample.
Detectors collect these X-rays, backscattered electrons and secondary electrons and convert them into a signal that is sent to a screen similar to a television screen. This produces the final image. The secondary emission of electrons (figure 2.10) from the specimen surface is usually confined to an area near the beam impact zone that permits images to be obtained at a relatively high resolution. These images as seen on a Cathode Ray Tube provide a three dimensional appearance due to the large depth of field of the SEM and the shadow relief effect of the secondary electrons contrast. Figure 2.9 represents the schematic diagram of SEM explaining the experimental set up.

A typical SEM has a working magnification range of from 10 to 100,000 diameters. A resolution can be attainable ~ 100 Å and a focus of 300 times that of an optical microscope. The large depth of field available with a SEM makes it possible to observe three-dimensional objects. The three-dimensional images produced allow different morphological features to be correctly interrelated and correctly analyzed. The unique advantage of Scanning Electrons Microscopy is that it does not need much samples loading activity and also, the thickness of the specimen is not a consideration. The surface of the sample may clean and smoothened before it is scanned. This helps in achieving better surface morphological and grain size information.
Figure 2.9: Diagram showing the working of Scanning Electron Microscope (SEM)

Figure 2.10: The outcomes of incident electron beam in a SEM
2.3.3 Transmission Electron Microscopy (TEM):

**Principle:**

TEM uses high energy electrons (up to 300 kV accelerating voltage) which are accelerated to nearly the speed of light. The electron beam behaves like a wavefront with wavelength about a million times shorter than lightwaves. When an electron beam passes through a thin-section specimen of a material, electrons are scattered. A sophisticated system of electromagnetic lenses focuses the scattered electrons into an image or a diffraction pattern, or a nano-analytical spectrum, depending on the mode of operation.

Each of these modes offers a different insight about the specimen. The imaging mode provides a highly magnified view of the micro- and nanostructure and ultimate, in the high resolution imaging mode a direct map of atomic arrangements can be obtained.

![The schematic outline of a TEM](image)

**Figure 2.11:** The schematic outline of a TEM
**Electron source:**

![Electron source diagram](diagram)

**Figure 2.12:** Electron source of TEM

The electron source consists of a cathode and an anode. The cathode is a tungsten filament which emits electrons when being heated. A negative cap confines the electrons into a loosely focused beam (Fig. 2.12). The beam is then accelerated towards the specimen by the positive anode. Electrons at the rim of the beam will fall onto the anode while the others at the center will pass through the small hole of the anode. The electron source works like a cathode ray tube.

**Electromagnetic lens system:**

After leaving the electron source, the electron beam is tightly focused using electromagnetic lens and metal apertures. The system only allows electrons within a small energy range to pass through, so the electrons in the electron beam will have a well-defined energy.

1. **Magnetic Lens:** Circular electro-magnets capable of generating a precise circular magnetic field. The field acts like an optical lens to focus the electrons.
2. **Aperture:** A thin disk with a small (2-100 micrometers) circular through-hole. It is used to restrict the electron beam and filter out unwanted electrons before hitting the specimen.
The sample holder is a platform equipped with a mechanical arm for holding the specimen and controlling its position.

**Imaging system:**

![Image of TEM imaging system](image)

**Figure 2.13:** Imaging system of TEM

The imaging system consists of another electromagnetic lens system and a screen. The electromagnetic lens system contains two lens systems, one for refocusing the electrons after they pass through the specimen, and the other for enlarging the image and projecting it onto the screen. The screen has a phosphorescent plate which glows when being hit by electrons. Image forms in a way similar to photography.

**Working principle:**

TEM works like a slide projector. A projector shines a beam of light which transmits through the slide. The patterns painted on the slide only allow certain parts of the light beam to pass through. Thus the transmitted beam replicates the patterns on the slide, forming an enlarged image of the slide when falling on the screen.

TEM work the same way except that they shine a beam of electrons (like the light in a slide projector) through the specimen. However, in TEM, the transmission of electron beam is highly dependent on the properties of material being examined. Such properties include density, composition, etc. For example, porous material will allow more electrons to pass through while dense material will allow less. As a result,
a specimen with a non-uniform density can be examined by this technique. Whatever part is transmitted is projected onto a phosphor screen for the user to see.

### 2.3.4 Atomic force microscopy (AFM):

Atomic force microscopy (AFM) is a high-resolution type of scanning probe microscopy, with demonstrated resolution on the order of fractions of a nanometer, more than 1000 times better than the optical diffraction limit. The AFM is one of the foremost tools for imaging, measuring, and manipulating matter at the nanoscale. The information is gathered by "feeling" the surface with a mechanical probe. Piezoelectric elements that facilitate tiny but accurate and precise movements on (electronic) command enable the very precise scanning. In some variations, electric potentials can also be scanned using conducting cantilevers. In newer more advanced versions, currents can even be passed through the tip to probe the electrical conductivity or transport of the underlying surface, but this is much more challenging with very few research groups reporting consistent data [16].

**Figure 2.14:** A commercial AFM setup (reproduced from ref. 17)

**Identification of individual surface atoms:**

The AFM can be used to image and manipulate atoms and structures on a variety of surfaces. The atom at the apex of the tip "senses" individual atoms on the
underlying surface when it forms incipient chemical bonds with each atom. Because these chemical interactions subtly alter the tip's vibration frequency, they can be detected and mapped. This principle was used to distinguish between atoms of silicon, tin and lead on an alloy surface, by comparing these 'atomic fingerprints' to values obtained from large-scale density functional theory (DFT) simulations [18].

The trick is to first measure these forces precisely for each type of atom expected in the sample, and then to compare with forces given by DFT simulations. The team found that the tip interacted most strongly with silicon atoms, and interacted 23% and 41% less strongly with tin and lead atoms, respectively. Thus, each different type of atom can be identified in the matrix as the tip is moved across the surface.

2.3.5 Magnetic force microscope (MFM):

Principle:

The magnetic force microscope (MFM) is a variety of atomic force microscope, where a sharp magnetized tip scans a magnetic sample; the tip-sample magnetic interactions are detected and used to reconstruct the magnetic structure of the sample surface. Many kinds of magnetic interactions are measured by MFM, including magnetic dipole–dipole interaction. MFM scanning often uses non-contact AFM (NC-AFM) mode.

In MFM measurements, the magnetic force between the sample and the tip can be expressed as

$$\vec{F} = \mu_0 (\vec{m} \cdot \vec{V}) \vec{H}$$

where $\vec{m}$ is the magnetic moment of the tip (approximated as a point dipole), $\vec{H}$ the magnetic field from the sample surface, and $\mu_0$ is the magnetic permeability of free space. Because the magnetic field from the sample can affect the magnetic state of the tip, and vice versa, interpretation of the MFM measurement is not straightforward. For instance, the geometry of the tip magnetization must be known for quantitative analysis. Typical resolution of 30 nm can be achieved.
**Schematic Diagram and Working:**

MFM block controller scheme. The laser beam is focused on the flexible cantilever. While the cantilever feels any stray field changes, the angle of the deflected light changes as well. Reflected light is registered by sensitive detector (four section photodiode PSPD) and transformed to the electric signal (organization known as the optical lever set-up).

![Schematic Diagram of MFM](image)

**Figure 2.15:** Schematic diagram of MFM

The MFM gets benefit from two basic detection principles, every for specific type of the magnetic interaction – static (DC) mode and dynamic (AC) mode.

- **Static (DC) mode:**
  
  In this regime cantilever carries over the magnetic force incidence as a product of the tip-sample interaction, where the rising displacement $\Delta z$ of the cantilever is measured (spring constant is denoted here as $k$) and thus in the area of elastic deformation obeys Hooke’s law

  \[ F = -k \Delta z \]

- **Dynamic (AC) mode:**
  
  This regime keeps up the cantilever at, or very close, to its resonance frequency. It is possible to construe the cantilever as a harmonic oscillator with the resonant frequency $f$, 
Here $m$ and $k_{ef}$ represent the effective mass and the effective spring constant for a whole system (tip + cantilever). Consequently the effective spring constant $k_{ef}$ falls into two components:

$$k_{ef} = k - \frac{\partial F}{\partial z}$$

where $k$ represents the cantilever spring constant and the derivative of the force $\partial F / \partial z$ (force gradient) with respect to tip-sample distance can be treated as an interaction spring constant, which is stationary only during one oscillation period. While the probe is approaching the sample surface, the derivative varies due to the mean tip-sample distance. Let us see how the force gradient changes the resonant frequency after the substitution of equations,

$$f = f_0 \sqrt{1 - \frac{\partial F / \partial z}{k}}$$

where $f_0$ is the free resonance frequency of the cantilever with respect to the condition of no tip-sample interaction. There are two ways to deal with resonance frequency measurement. The amplitude detection is Modeled tip-sample interaction, where $k$ denotes cantilever constant and the force derivative $\partial F / \partial z$ is schematically depicted here as an additive force interaction constant.

**Figure 2.16:** Tip motion of the MFM
There are two ways to deal with resonance frequency measurement.

Amplitude detection and frequency detection. The amplitude detection is based on the cantilever oscillated at a given frequency (its value is greater than the free resonant frequency), which means the changes in resonant frequency cause deflections of the cantilever. The frequency detection can be realized as follows: the cantilever is vibrated accurately at its resonant frequency f where the amplitude is controlled by the feedback loop. Resulting detection is assured by an FM demodulator. With respect to the fact that MFM can be operated in constant frequency shift mode, two-pass (tapping-lift) mode or constant height mode, the crucial issue is to minimize surface topography features on the image of the magnetic force distribution. To solve this problem, the major part of the MFM measurements is performed in terms of two-pass mode.

![Figure 2.17: Mode of scanning of MFM](image)

**Imaging samples:**

The MFM can be used to image various magnetic structures including domain walls (Bloch and Neel), closure domains, recorded magnetic bits, etc. Furthermore, motion of domain wall can also be studied in an external magnetic field. MFM images of various materials can be seen in the following books and journal publications: [5, 6, 18] thin films, nanoparticles, nanowires, permalloy disks and recording media.
**Advantages:**

The popularity of MFM originates from several reasons, which include:

- The sample does not need to be electrically conductive.
- Measurement can be performed at ambient temperature, in ultra-high vacuum (UHV), in liquid environment, at different temperatures, and in the presence of variable external magnetic fields.
- Measurement is nondestructive to the crystal lattice or structure.
- Long-range magnetic interactions are not sensitive to surface contamination.
- No special surface preparation or coating is required.
- Deposition of thin non-magnetic layers on the sample does not alter the results.
- Detectable magnetic field intensity, $H$, is in the range of 10 A/m.
- Detectable magnetic field, $B$, is in the range of 0.1 gauss (10 micro-tesla).
- Typical measured forces are as low as $10^{-14}$ N, with the spatial resolutions as low as 20 nm.
- MFM can be combined with other scanning methods like STM.

**Limitations:**

There are some shortcomings or difficulties when working with an MFM, such as:

- The recorded image depends on the type of the tip and magnetic coating, due to tip-sample interactions.
- Magnetic field of the tip and sample can change each other's magnetization, $M$, which can result in nonlinear interactions. This hinders image interpretation.
- Relatively short lateral scanning range (order of hundreds micrometers).
- Scanning (lift) height affects the image.
- Housing of the MFM system is important to shield electromagnetic noise (Faraday cage), acoustic noise (anti-vibration tables), air flow (air isolation), and static charge on the sample.
2.4 Transport and Magneto transport Characterization:

The knowledge about the electrical properties of the bulk materials, thin films and artificial devices is essential in determining their applicability and usefulness. The resistivity must be measured accurately since its value is critical from application point of view. The samples in the present thesis work were characterized for their electrical and magneto transport properties by the DC four-probe resistivity technique as described below.

2.4.1 Four Probe D. C. Resistivity (Without and With Applied Magnetic Field):

The dc resistivity of a sample is measured by the voltage drop across a specimen when a current of known magnitude, which is typically around 1 mA, passes. The terminals used for measuring the voltage pass little current when connected to a high impedance voltmeter. These terminals are distinct from those used for passing the main part of the current through the specimen, where voltage drops in both leads and contacts are significant. The figure 2.18 shows a schematic diagram of four probes connected to a specimen whose temperature is measured by a temperature sensor in thermal contact with the specimen [19].

The resistivity measured is not necessarily a bulk property. Provided applied currents are small, one fiber of superconducting region in a specimen may give rise to a resistivity discontinuity typical of superconducting transition. Conversely, circuits can be broken by cracks and contact failure caused by thermal stress arising during a measurement. These can cause discontinuities in the voltage signal, which may give the illusion of superconductivity, but which can usually be checked by monitoring the simultaneous current flow.

A similar four-probe apparatus can be used for elementary measurements of \( J_c \), defined according to the sensitivity of the apparatus or to a selected criterion. In bulk material, the specimen, e.g., \( \text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3 \) is mounted on a thermally compatible, insulating substrate (say quartz film) for mechanical strength. The contacts must have low resistance to reduce heating effects. The heating effect of the high currents at contacts and neck is further reduced by use of a pulsed current source. Starting with a low current, this is increased until the voltage drop, observed with a
rapid voltage monitor, such as an oscilloscope, reaches a defined level corresponding to $E_c$.

**Figure 2.18:** Schematic diagram of a four-probe setup

AC resistivity can be measured by a similar four-probe arrangement, but using an AC current source and lock-in amplifier for voltage measurement. Signal noise is reduced by the use of a preamplifier close to the specimen. Alternatively, if a specimen is biased with voltage $V$ and microwave ac frequencies $\nu$ applied across a junction, the ac Josephson effect is observed.

### 2.4.2 Current vs. Voltage (I-V) measurements:

Since last few years the efforts have been made on the fabrication of devices based on oxide thin films and multilayers, having potential applications. To understand the transport behavior of such single crystalline and polycrystalline thin film and devices, I-V characteristics emerge as a most comprehensive tool. In addition, many important parameters can be extracted from I-V measurements. For practical application of the insulating oxide films, the leakage current controls the charge retention property which is very important affecting factor for the consideration in practical memory application.
During the present work, the I-V behavior of the oxide thin film heterostructures & p-n junction diodes was studied using the DC two probe method by varying the applied voltage and observing the variation in current. Figure 2.12 show the schematic of contact geometry used in the I-V measurements. All the measurements were taken from the Ag electrodes. For multiferroic thin films, hysteretic I-V measurements were taken at various temperatures and varying ±V_max. Effect of doping concentration and thickness variation has been studied on behavior of I-V curves.

2.4.3 Capacitance – Voltage (C-V) Measurement:

Capacitance–voltage characterization is a technique for characterizing semiconductor materials and devices. The applied voltage is varied, and the capacitance is measured and plotted as a function of voltage. The technique uses a metal–semiconductor junction (Schottky barrier) or a p–n junction [20] or a MOSFET to create a depletion region, a region which is empty of conducting electrons and holes, but may contain ionized donors and electrically active defects or traps. The depletion region with its ionized charges inside behaves like a capacitor. By varying the voltage applied to the junction it is possible to vary the depletion width. The dependence of the depletion width upon the applied voltage provides information on the semiconductor's internal characteristics, such as its doping profile and electrically active defect densities [21, 22]. Measurements may be done at DC, or using both DC and a small-signal AC signal (the conductance method [22, 23]), or using a large-signal transient voltage [24]. To understand the C-
V characteristics of prepared film electrode connected as shown in figure 2.13 in which electrode prepared using fine silver paste.

**Figure 2.17:** Schematic diagram of electrode preparation on thin film for C-V measurement.
References:


