2.1 INTRODUCTION

Thin film is defined as a low dimensional material with a thickness < 1 micron created by condensing atomic or molecular or ionic species of matter one by one. Materials in the form of thin films have been extensively used in physical research and device applications (Wasa et al 2004). The basic properties of thin films such as composition, crystal phase and orientation, film thickness and microstructure are controlled by deposition conditions. Thin film properties strongly depend upon the method of deposition, substrate material or orientation, substrate temperature, rate of deposition and background pressure. The applications and the properties of the given material determine the most suitable technique for the preparation of the thin films of that material.

2.2 THIN FILM PREPARATION TECHNIQUES

In general, any thin film deposition follows the sequential steps: a source material is converted into the vapour form (atomic/molecular/ionic species) from the condensed phase of solid or liquid, which is transported to the substrate and then it is allowed to condense on the substrate surface to form the solid film (Goswami 1996). Depending on how the atoms or molecules or ions or clusters of species are created for the condensation process, the deposition techniques are broadly classified into two categories: physical methods and chemical methods. Chemical bath deposition, chemical vapour deposition and spray pyrolysis are examples of chemical method of thin film deposition. Thermal evaporation, electron beam evaporation, RF or
Direct Current (DC) sputtering and PLD are examples of physical methods. Metal oxide compounds in the form of thin films are most successfully developed by physical methods. For the present research, pure and Ca modified BMO thin films have been grown by RF magnetron sputtering. The electrodes for the electrical studies have been deposited using thermal evaporation technique.

2.2.1 Sputtering

Sputtering is one of the most versatile techniques used for the deposition of thin films of device quality. The sputtering process produces better films with controlled composition, greater adhesion, homogeneity and permits better control of film thickness. This process involves the creation of gas plasma usually of an inert gas such as argon (Ar), krypton (Kr) and so on (Smith 1995) by applying voltage between cathode and anode. The target material which is to be coated acts as cathode and the substrate on which the material to be coated acts as anode. The source material is subjected to the bombardment of energetic inert gas ions. By momentum transfer, particles are ejected from the surface of the cathode and they diffuse away from it, depositing a thin film onto a substrate.

Sputtering is normally performed at a pressure of $10^{-2} - 10^{-3}$ Torr. In sputtering system, the plasma is created by two methods: DC and RF biasing. In DC sputtering, a direct voltage is applied between cathode and anode. This method is restricted to conducting targets only. RF sputtering is suitable for both conducting and non-conducting targets.

In RF sputtering, a high frequency potential of 13.56 MHz has been directly applied between the metal electrodes behind the target and substrate holder. Figure 2.1 shows the schematic representation of RF sputtering system. When the RF generator is turned on, an alternating electric field is developed.
In the first phase of the alternating voltage, as the target is biased at a higher potential compared to the substrate, any electrons present in the chamber (due to background radiation or electron emission from the target surface as a result of the large potential difference between the electrodes) are accelerated towards the substrate. These accelerated electrons collide with the Ar gas atoms on their way. The Ar atoms gain energy due to the collision and excite to higher state. The excited atoms are ionised into Ar\(^+\) ions and additional electron. The excited Ar\(^+\) ions quickly decay to their ground state with the emission of photon resulting in the formation of a glow discharge. The generated Ar\(^+\) ions by ionisation are attracted towards the target where they collide with the target surface, knocking off material atoms and generate electrons. These secondary electrons are again accelerated towards the substrate. This leads to more collisions and ionisation, hence the plasma is sustained. Thus, the knocked atoms from the target surface are condensed on the substrate surface.

Sputtering yield has been improved by using magnetic fields and is referred to as DC or RF magnetron sputtering. In the RF magnetron sputtering, the magnetic field from the magnets beneath the target increases the path of the electrons in the plasma and amplifies the gas ionisation as the electron collides with more gas atoms. In addition, the magnetic fields trap the electrons to the vicinity of the target and keeps away from the substrate. Hence film damage and substrate heating due to energetic electrons collision have been avoided. It also reduces the sputtering of atoms from the walls of the chamber that could contaminate the film. In reactive sputtering, the reactive gas is admitted into the sputtering chamber along with argon. The deposition rates and properties of the films strongly depend on the sputtering conditions such as the partial pressure of the reactive gas, sputtering power, the sputtering pressure, substrate temperature and target to substrate distance.
Figure 2.1  Schematic view of sputtering chamber

Figure 2.2  RF Magnetron sputtering Unit (Model VR SPU 06D)
In sputter deposition, the atom diffuses around the substrate with a motion determined by its binding energy to the substrate, which is determined by the nature and temperature of the substrate. Depressions on the substrate surface act as adsorption sites for diffusing atoms. At each hop, the atom would either jump over the barrier into an adjacent site or would re-evaporate. After some time, the atom would either evaporate from the surface or would join with another diffusing single atom to form a doublet. These doublets would be joined by the other single atoms to form triplets, quadruplets and so on. This stage is known as the nucleation stage of thin film growth and it leads to the formation of quasi-stable islands. The islands would grow in size and lead to the coalescent stage which proceeds until the film reaches continuity. Sputter yield (S) of the film is calculated using the given ratio.

\[ S = \frac{\text{Number of sputtered atoms}}{\text{Number of incident ions}} \]

This sputter yield depends upon the type of target atom, binding energy of target atoms, crystal structure of the target surface, relative mass of ions and atoms, incident ion energy and angle of incidence of ions.

### 2.2.1.1 Operating Parameters

Glow discharge in sputtering is widely dependent on the work function of the target material and pressure of the environmental gas. The sputter head and sputter power supply should be effective over a range of anticipated target materials. The deposition rate is current dependent and if it is operated in the correct glow region of the plasma discharge, several fold changes in current should be available for a relatively small change in sputtering voltage. The deposition rate should not be sensitive to small changes in pressure inside the chamber. Argon has a relatively high atomic weight which provides a suitable source of ions for effective bombardment of
the target material. Sputtering in air should be avoided. The effectiveness of sputtering is also dependent on the "mean free path" (m.f.p.), which is inversely proportional to pressure. If the m.f.p. is too short, insufficient energy will be gained for effective bombardment and it will reduce the movement of the sputtered material from the target, but if the m.f.p. is too long, insufficient collisions with the target atoms will occur. The role of sputtering parameter is significant on the film properties.

In the film growth, substrate is being bombarded by electrons and ions from target and plasma, neutral atoms deposit independently, which can be controlled by putting small negative bias on the substrate. The substrate temperature is controlled by substrate heater. Particle energy increases with the increasing sputter voltage, but decreases with the increasing substrate bias and increasing Ar pressure. The typical operating parameters of RF magnetron sputter coater are given in Table 2.1.

**Table 2.1 Typical operating parameters of RF sputter coater**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum pressure</td>
<td>2×10⁻² to 8×10⁻² mbar</td>
</tr>
<tr>
<td>RF power</td>
<td>0-600 W</td>
</tr>
<tr>
<td>Deposition</td>
<td>0-25 nm/ min</td>
</tr>
<tr>
<td>Grain size</td>
<td>Less than 5 nm</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>0 - 1200 °C</td>
</tr>
<tr>
<td>Target-substrate distance</td>
<td>4-8 cm</td>
</tr>
</tbody>
</table>

**2.2.1.2 Advantages of Sputtering**

The following are the advantages of sputtering techniques.

i. Cannot a line of sight method

ii. Can use diffusive spreading for coating films

iii. Can coat around corners of substrate
iv. Can process alloys and compounds
v. Does not need high temperatures
vi. Sputters even organic compounds
vii. Can coat large areas more uniformly
viii. Need large target sources and less maintenance
ix. Can control film thickness by varying the deposition time.

### 2.2.1.3 Fabrication of Target

Targets used for the growth of BiMnO$_3$ and Bi$_{1-x}$Ca$_x$MnO$_3$ (0.1 $\leq$ x $\leq$ 0.4) films are prepared by conventional solid state reaction route. The Bi (10 at.%) rich pellets are fashioned by mixing the primary oxide powders, Bi$_2$O$_3$ (99.99 % pure) and MnO$_2$ (99.95 % pure) for BiMnO$_3$; Bi$_2$O$_3$ (99.99 % pure), CaO (99.90 % pure) and MnO$_2$ (99.95 % pure) for Bi$_{1-x}$Ca$_x$MnO$_3$. The intentional adding of Bi is to compensate the high Bi volatility; otherwise Bi deficient films may be produced. These powders are purchased from Alfa Aesar. The target fabrication process consists of several steps as listed below.

i. The powders are weighted according to the stoichiometry needed for BiMnO$_3$ and Bi$_{1-x}$Ca$_x$MnO$_3$. 10 at. % excess amount of Bi$_2$O$_3$ is added in order to compensate the high Bi volatility.

ii. The powders are ground for 5-6 hours with an aim to homogenize the oxides and to reduce the volume of the powder particles so as to maximize the surface of them.

iii. The mixture is pressed into a pellet of 2 inch dia and 2-3 mm thickness in a slow continuous process by applying 200 kN pressure using universal testing machine.

iv. The pressed pellet has been temperature treated inside an
alumina crucible upto 500 °C for 6 hours (with a 10 °C/ minute increasing and decreasing ramps).

v. The pellet is again homogenized and step (ii) and (iii) are repeated. Then the thermal treatment is applied as in step (iv) but upto 600 °C for 6 hours.

vi. Finally, the processes (ii), (iii) and (iv) are repeated for the third time, but with a thermal annealing of 700 °C for 6 hours. The repetition of this process ensures the achievement of homogeneous and dense target as possible.

2.2.2 Thermal Evaporation

Thermal evaporation is the most widely used technique for the preparation of thin films of metals, alloys and many other compounds. In a vacuum environment, sufficient amount of heat is given to the evaporants to reach the vapour pressure necessary for the evaporation. The evaporated material is allowed to condense on a substrate kept at a suitable temperature. When the evaporation is made in vacuum, the evaporation temperature would be considerably lower and the formation of the oxides and the incorporation of impurities in the growing layer would be reduced. Evaporation is normally done at a pressure of $10^{-5}$ Torr. At this pressure, a straight line path for most of the vapour atoms is ensured for a substrate-source distance of nearly 10 cm (Chopra & Kaur 1969). The characteristics and the quality of the deposited film would depend on the substrate temperature, rate of deposition, ambient pressure and so on. The uniformity of the film depends on the geometry of the evaporation source and its distance from the source. This deposition by thermal evaporation is simple, convenient and is widely used (Holland 1970). Thermal evaporation by resistive heating has been used for the deposition of metal electrodes in the present study as illustrated in Figure 2.3.
Figure 2.3  Thermal evaporation unit (Model: 12A4D)
2.3 CHARACTERIZATION TECHNIQUES

2.3.1 X-ray Diffraction (XRD)

2.3.1.1 Theory

Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. XRD is a versatile and a non-destructive technique used primarily for determining crystal structure, lattice parameters, phase identification, texture of the film, epitaxial relation with the substrate and so on. It is based on constructive interference of monochromatic X-rays after interacting with crystalline sample.

X-rays are generated in a Coolidge tube and are directed onto the sample. A detector detects the reflected X-ray signal which is then processed either by a microprocessor or by electronically converting the signal to a count rate. The detector signal is recorded by changing the incident angle of the X-rays. The schematic diagram of the XRD process is shown in Figure 2.4. This technique is based on the interference pattern produced by a monochromatic incident rays when interacting with a periodic structure of the ions in a crystalline material forming atomic planes as shown in Figure 2.5. For a given family of planes (hkl), interplanar distance (d_{hkl}), constructive interference occurs when the incident angle θ is such that it attains the path difference of two waves that equals a multiple of the wavelength of the incoming radiation, the so-called diffraction condition of Bragg’s law (Cullity 1978),

\[ n\lambda = 2d_{hkl}\sin\theta \]  \hspace{1cm} (2.1)

where the integer n is the order of the diffracted beam and λ is the wavelength of the incident X-ray beam (λ = 1.5406Å for Kα line of copper). The diffracted
X-rays are then detected, processed and counted. By scanning the sample through a range of 2θ angles (10°-80°), all the possible diffraction directions of the lattice could be attained due to the orientation of the material. Thus, the obtained XRD pattern contains a set of lines or peaks, each of different intensity and position (d-spacing or Bragg angle, 2θ).

Figure 2.4  Schematic illustration of XRD analysis

Figure 2.5  Representation of Bragg’s law (Langenberg Perez 2013)
For a given substance, the line positions are basically fixed by crystal structure, lattice parameters and characteristic of that substance. The intensity of peaks may vary based on the orientation of the grains. Each crystalline substance has its own characteristic diffraction pattern, which is used for phase identification. The identification of the phases present in an unknown sample using the diffraction technique is based on the comparison of the diffraction pattern of the unknown mixture with a diffraction file collected and maintained by Joint Committee on Powder Diffraction Standards at the International Centre for Diffraction Data (JCPDS-ICDD). The XRD quantitative analysis is based on the premise that each crystalline phase in a mixture has a unique diffraction pattern, and the intensity of the peak varies directly with its concentration (Kaufmann 2003)

2.3.1.2 Applications

XRD analysis has wide applications, some of which are listed below.

i) Pharmaceutical industry: Used to unambiguously characterize the composition of pharmaceuticals.

ii) Forensic science: Used mainly in contact trace analysis.

iii) Geological applications: Used as a key tool in mineral exploration.

iv) Microelectronics industry: The silicon and gallium arsenide are used in integrated circuit production as a substrate. These materials have to be characterized by XRD for its purity, orientation and so on.
v) Glass industry: Used to study the glass materials.

2.3.2 Scanning Electron Microscopy (SEM)

A Scanning Electron Microscope (SEM) is a powerful magnification tool that utilizes focused beams of electrons to obtain the morphological information. The schematic diagram of SEM microscope is shown in Figure 2.6.

2.3.2.1 Working

![Schematic drawing of SEM]

Figure 2.6 Schematic drawing of SEM

High energy electrons are emitted from an electron gun fitted with a tungsten filament cathode. These electron beams are narrowed by limiting
aperture and condenser lens. After the beam passes through pairs of scanning coils in the electron column, typically in the final lens (objective lens), which deflect the beam in the x and y axis, it scans in a raster fashion over a rectangular area of the sample surface. The operating voltage used in SEM is much smaller than that of TEM, so that the electron beam interacts with the sample surface layer about several microns deep.

When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering. The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by different detectors. The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current.

2.3.2.2 Applications

SEM is used to analyze the surface morphology and surface features of the powder and thin film samples.

2.3.3 Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) provides a three dimensional surface profile, which permits the determination of the roughness of the sample. It works in room pressure and the samples need not be covered with a conducting coating. It measures the force between the tip, which is attached with the cantilever and the surface of the sample. The positive or negative bending of the cantilever is observed by the attractive or repulsive forces. AFM has a different operation mode for characterizing the sample.
2.3.3.1 Working

AFM consists of a micro scale cantilever with a sharp tip at its end that is used to scan the sample surface. When the tip is moved close to the surface of the sample, short-range forces (as Vander Waals) between the tip and the sample surface appear which leads to the deflection of the cantilever according to Hooke's law. Typically, the deflection is measured using a laser spot reflected from the top surface of the cantilever using an array of photodiodes. The schematic representation of AFM is shown in Figure 2.7. The constant force between the probe and the sample surface is maintained by the feedback mechanism. When the probe signal decreases, the circuit realizes that the surface is now far away, it moves the probe down until the signal increases to the same level measured at the previous point. Similarly, the circuit responds to the increased probe signal by moving the probe up and away from the surface, until the signal decreases back to the desired level. These measured cantilever deflections are used to generate a map of the surface topography of the sample.

AFM can be operated in a number of modes depending on the application. In general, possible imaging modes are divided into static (also called contact) modes and a variety of dynamic (non-contact or tapping) modes where the cantilever is vibrated.

2.3.3.2 Applications

AFM is mainly used for

i) Surface roughness analysis

ii) Step formation in thin film epitaxial deposition

iii) Pin-hole formation or other defects in oxide growth
iv) Grain size analysis

v) Phase mode is very sensitive to variations in material properties including surface stiffness, elasticity and adhesion.

2.3.4 X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS), also known as electron spectroscopy for chemical analysis is based on the photoelectric effect. The X-ray photoelectron is an electron ejected from the inner electron shell of an atom when the atom absorbs an X-ray photon as shown in Figure 2.8. An incident X-ray can have sufficient energy ($h\nu$) to knock out an inner shell electron, for example from $K$ shell of the atom. In such a case, the K-shell electron would be ejected from the surface as a photoelectron with kinetic
energy ($E_K$). Knowing the value of $E_K$, the binding energy ($E_B$) of the atom’s photoelectron is calculated using the following relation (Leng 2009).

$$E_B = h\nu - E_K - \phi$$  \hspace{1cm} (2.2)

where $\phi$ is the parameter representing the energy required for an electron to escape from a material’s surface (work function), $h$ is Planck’s constant and $\nu$ is the frequency. The value of $\phi$ depends on both the sample material and the spectrometer. The $E_B$ of atomic electrons have characteristic values which are used to identify the chemical elements present in the sample. Moreover, as the energy detector quantifies the number of arriving electrons, XPS is also quantitative. In addition, the exact $E_B$ of an electron not only depends on the level from which photoemission is occurring but also on the formal oxidation state of the atom and the local chemical and physical environment. XPS can be used to determine the valence of the elements in the sample.

A typical XPS spectrum is a plot of intensity versus binding energy. Photoelectrons are ejected from different electronic shells and subshells. Each $E_B$ peak is marked as an element symbol with a shell symbol from where the photoelectron is emitted like Al-2p, O-1s as shown in Figure 2.9. The photoelectrons emitted by subshells p, d and f are usually marked with an additional fraction number; Mn-2p$_{1/2}$, Mn-2p$_{3/2}$ where 1/2 and 3/2 for the p subshell, 3/2 and 5/2 for the d subshell and 5/2 and 7/2 for the f subshell. These fractions represent the quantum number of total angular momentum ($J$) for an individual shell electron. The XPS spectrum may also have peaks from Auger electrons.

2.3.4.1 Instrumentation

The three basic components of XPS are: (i) X-ray source, (ii) spectrometer and (iii) high vacuum. Figure 2.10 illustrates the schematic
representation of XPS system. X-ray line widths are proportional to the atomic number of the target in the X-ray tube. The X-ray line width in XPS should be as narrow as possible, hence light elements like Al ($E_{K\alpha} = 1.4866$ keV) or Mg ($E_{K\alpha} = 1.2566$ keV) are common X-ray sources. Some XPS systems are equipped with multiple anode X-ray sources.

![Diagram of characteristic electron emission](image)

**Figure 2.8** Emission of characteristic electrons: (a) 1s Photoelectron (b) $K_{L1, L2, 3}$ Auger electron (Leng 2009).

![XPS spectrum of an oxidized aluminum surface](image)

**Figure 2.9** XPS spectrum of an oxidized aluminum surface (Watts & Wolstenholme 2003).
X-ray generation from low atomic number materials also has reduced background radiation. The primary X-rays may be filtered by crystal dispersion to remove X-ray satellites and continuum radiation, but this filtering reduces the X-ray intensity substantially. The XPS electrons are detected by one of the types of detectors. The hemispherical sector analyzer consists of two concentric hemispheres with a voltage applied between them.

![Figure 2.10 Schematic construction of XPS system](image)

A spectrum is generated by varying the voltage so that the electron trajectories with different energies are brought to a focus at the analyser exit slit. An electron multiplier amplifies the signal. Chemical compounds or elements are identified by the location of energy peaks on the undifferentiated XPS spectrum. Peak heights and peak areas can be used with appropriate correction factors to obtain densities, but XPS is primarily used for the identification of elements (Schroder 2006). A modern instrument for electron spectrometry contains both XPS and Auger Electron Spectroscopy (AES) in a single chamber as a multifunctional surface analysis system. A SEM system may also be included in order to image the microscopic area to be examined by electron spectroscopy.

### 2.3.4.2 Applications

XPS is used to analyse the chemical surface information and the oxidation states of the elements in organics, polymers and oxides. It has been
extensively used in the semiconductor industry for solving a variety of problems. It has played a major role in understanding the chemistry and reaction mechanisms in the development of plasma etching. It has been applied to die attachment problems, adhesion of resins to metal surfaces and inter diffusion of nickel through gold. Recently, it has found its use in oxide thickness measurements (Schroder 2006).

2.3.5 Vibrating Sample Magnetometer (VSM)

2.3.5.1 Instrumentation

Vibrating Sample Magnetometer (VSM) is used to measure the magnetic properties of the films. When a sample is placed in a homogeneous magnetic field, a magnetic moment is induced in the sample. If this sample is made to undergo sinusoidal motion, i.e. mechanically vibrated, the vibration induces a magnetic flux change. This in turn induces a voltage in the pick-up coils. Figure 2.11 shows a typical VSM set up.

The sample is suspended from a vibrating drive head by a non-magnetic rod and placed between two electromagnets which produce a DC magnetic field. The vibrator generates a vertical sinusoidal vibration with a frequency of 82 Hz. Therefore, the sample experiences sinusoidal motion, which induces an electrical signal in the coils mounted on the pole faces of the electromagnets. The signal picked up by the coils is proportional to the frequency and amplitude of the sinusoidal motion, and to the total magnetic moment of the sample at the applied magnetic field. The frequency and amplitude of the sinusoidal motion are maintained constant by a capacitor (reference signal generator). By feeding the signals from the pick-up coils and the reference signal into a demodulator, the magnetic moment of the sample is extracted based on Faraday’s law; an emf would be generated in a coil when
there is a change in the flux that goes through the coil. For a coil with \( n \) turns of cross-sectional area \( A \), the emf (V) is related to \( \frac{dB}{dt} \) given as

\[
V = -n a \frac{dB}{dt}
\]  

(2.3)

Since \( \Delta B = \mu_0 M \), when a magnetic sample is placed into the coil, this relationship becomes \( V = \frac{-n a \mu_0 M}{dt} \) (Wang 2005). The magnetic moment determined by VSM is given in terms of the basic electromagnetic unit (emu/cc), which can be related to the magnetization, susceptibility and Bohr magneton. VSM provides a fast and easy way for measuring the magnetic properties of materials.

---

**Figure 2.11** Schematic diagram of VSM set up
2.3.5.2 Applications

VSM has been used for magnetic measurements as a function of temperature and field of ferromagnetic, ferrimagnetic, antiferromagnetic, paramagnetic and diamagnetic materials. The magnetic properties of the materials such as demagnetising factors, anisotropy, magnetization processes and magnetic saturation can be easily demonstrated.

2.3.6 Dielectric Measurements

Dielectric materials are used to store electrical energy. When a dielectric is placed in an electric field, electric charges do not flow through the material as they do in a conductor, but they only shift slightly from their average equilibrium positions causing dielectric polarization (P). Due to dielectric polarization, positive charges are displaced towards the field while negative charges shift in the opposite direction creating an internal electric field which reduces the overall field within the dielectric itself.

Dielectric materials are used in many applications from simple electrical insulation to sensors and circuit components. The dielectric constant ($\varepsilon_r$) of a material is defined as the ratio of permittivity of the medium ($\varepsilon$) to permittivity of the free space ($\varepsilon_0$) as given in Equation (2.4).

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0}$$

(2.4)

$\varepsilon_r$ is the dielectric constant or relative permittivity of the medium. The measure of dielectric constant or relative permittivity gives the properties of a dielectric material. When an alternating current (ac) field is applied to a dielectric material, some amount of electrical energy is absorbed by dielectric material and is dissipated in the form of heat. This loss of energy is known as dielectric loss. This loss is high especially around the relaxation or resonance
frequencies of the polarization mechanisms as the polarization lags behind the applied field, causing an interaction between the field and the dielectric polarization that result in heating. In an ideal dielectric material, the current leads the voltage by an angle of 90°, but in the case of a commercial dielectric, the current does not exactly lead the voltage by 90°. It leads by some other angle θ that is less than 90°. The angle $\phi = 90° - \theta$ is known as the dielectric loss angle. For a dielectric, having capacitance (C) and voltage (V) applied to it at a frequency (Hz), the dielectric power loss is given by

$$P = jV^2 \omega C \tan \phi$$  

(2.5)

where $\tan \phi$ is said to be the power factor of the dielectric. The power loss depends only on the power factor of the dielectric, as long as the applied voltage, frequency and capacitance are kept constant.

### 2.3.6.1 Preparation of Sample for Electrical Measurements

Thin film samples are prepared in the described manner to measure significant dielectric and ferroelectric parameters, i.e. $\varepsilon$ and $P$ of multiferroic thin films as a function of applied electric field. Plane-parallel capacitor is the most suitable geometry for the measurement of dielectric permittivity and polarization in thin films. The measured dielectric/ferroelectric material of thickness $t$ is embedded in between two equal electrodes with a defined area $A$, which are parallel.

Gold (Au) top electrodes (circular dia ~ 0.5 mm and thickness of ~100 nm) are deposited by thermal evaporation through a shadow mask. This Au has been chosen because it is easy to be grown without impurities, but difficult to be degraded. Before Au growth, the sample is cleaned with acetone and ethanol and subsequent exposition to an ozone atmosphere. Figure 2.12 shows the sketches of electrical measurements.
2.3.6.2 Instrumentation

An LCR meter is a piece of electronic test equipment used to measure the Inductance (L), Capacitance (C) and Resistance (R) of a component.

2.3.6.3 Open Circuit and Short Circuit Compensation

Residual impedance component of the test fixture can be considered in terms of an equivalent circuit as shown in Figure 2.13. Further, the measured value $Z_m$ for impedance includes this residual component, and hence in order to obtain the genuine impedance value, it is necessary to compensate the measured value in terms of the open circuit impedance residual component and the short circuit residual component, which must be obtained accordingly. In the figure below, $Z_x =$ true value, $L_s =$ residual inductance, $C_0 =$ floating capacitance value, $Y_0 =$ open circuit residual component, $R_s =$ residual resistance, $G_0 =$ residual conductance, $Z_s =$ short circuit residual component and $Z_m =$ measured value.
The $Z_m$ is given by

$$Z_m = Z_s + \frac{1}{Y_0 + \frac{1}{Z_x}} \quad (2.6)$$

To obtain open circuit compensation, the terminals of the test fixture are left separated (open circuited). As the short circuit residual component $Z_s$ becomes zero, the open circuit residual component $Y_0$ can be determined. To obtain the short circuit compensation, the terminals of the test fixture are connected together (short circuited). As the open circuit residual component $Y_0$ is gets to zero, the short circuit residual component $Z_s$ can be determined. Thus obtained residual components, are recorded as compensation values and the compensation process may then be performed by substituting them into Equation (2.6).

2.3.6.4 Testing Parameters and Equations

Normal circuit elements are assessed with regard to their characteristics in terms of their impedance $Z$. LCR meter subjects such circuit
components to an ac signal at a certain test frequency, measures their voltage and current vectors and obtains the impedance $Z$ and the phase angle $\theta$ values. It is then possible to obtain the following quantities from the impedance $Z$ by displaying it upon the complex plane.

Moreover, it is possible to use the admittance $Y$ as a characteristic of a circuit component which is the reciprocal of the impedance $Z$. By displaying the admittance $Y$ upon the complex plane (as is done for the impedance $Z$) the following quantities can be obtained. The Figure 2.14 shows these quantities: $Z = \text{impedance (}\Omega), \theta = \text{phase angle (degrees)}, R = \text{resistance (}\Omega), X = \text{reactance (}\Omega), |Z| = \text{absolute value of impedance (}\Omega), Y = \text{admittance (}\text{S}), G = \text{conductance (}\text{S}), B = \text{susceptance (}\text{S})$ and $|Y| = \text{absolute value of admittance (}\text{S})$. From the voltage $V$, which is applied between the terminals of the sample under test, the current $I$ which flows through the test sample, the phase angle $\theta$ between $V$ and $I$, and the angular velocity $\omega$ which corresponds to the test frequency, the LCR meter can calculate the following components by using Equations [(2.7) - (2.12)] shown below.

\[
|Z| = \frac{V}{I} = \sqrt{R^2 + X^2} \quad (2.7)
\]

\[
|Y| = \frac{1}{|Z|} = \sqrt{G^2 + B^2} \quad (2.8)
\]
\[ B = |y| \sin \phi \]  
\[ C_p = \frac{B}{\omega} \]  
\[ \varepsilon_r = \frac{C_p t}{\varepsilon_0 A} \]  
\[ D = \frac{1}{|\tan \theta|} \]

where \( C_p \) is the parallel-equivalent static capacitance and \( D \) is the dielectric loss. The dielectric constant (relative permittivity) can be determined by using Equation (2.11).

2.3.6.5 **Applications**

Dielectric measurements are applied mainly

i. To determine frequency dependent dielectric constant and loss

ii. To determine the energy storing capacity of materials

iii. To measure temperature dependent dielectric studies so as to determine the ferroelectric \( T_c \).

2.3.7 **Ferroelectric Test**

Ferroelectric properties of the materials can be analyzed using standardised ferroelectric test system which has the features of function generator, an electrometer and a digital oscilloscope in a single package. The tester is controlled by the computer and the data is collected and displayed in screen using interface. This tester is working under the basic Sawyer-Tower circuit (Sawyer & Tower 1930) as shown in Figure 2.15.
2.3.7.1 Working Principle

In this experiment, the voltage is cycled by the signal generator. The voltage across the reference capacitor is measured when the direction of the ferroelectric material’s dipole is reversed at high frequency. Due to the series connection, the charge on the capacitor must be the same as the charge over the ferroelectric capacitor. This charge on the ferroelectric can be obtained by

$$Q = CV$$  \hspace{1cm} (2.13)$$

where $C$ is the capacitance of the reference capacitor and $V$ is the voltage measured over this capacitor. The measured polarization can be given by

$$P = \frac{Q}{A}$$  \hspace{1cm} (2.14)$$
where $Q$ is the charge developed on the plate (coulomb) and $A$ is the area of the plates ($\text{cm}^2$). Hence polarization of the material in an oscillating electric field can be represented by plotting the voltage applied to the material on the X-axis of the oscilloscope and the surface charge on the Y-axis. This can be done because the capacitance of the reference capacitor is much higher than that of the ferroelectrics and so most of the voltage lies over the ferroelectric range. It is only possible to measure $P$ by cycling the polarization through cycling the voltage across the ferroelectric. The absolute values can get deduced from the changes measured when cycling the polarization.

### 2.3.7.2 Applications

The features of ferroelectric measurement are

i. To study the ferroelectric behaviour of the materials

ii. To find the values of $P_r$, $P_s$ and $H_c$ of the ferroelectric materials

iii. To study the fatigue behaviour of the ferroelectric materials.