Chapter 2

Synthesis and characterization techniques
In this chapter, details about the experimental techniques employed during the course of work will be discussed. This chapter has been arranged in the following way: First we describe about the sample synthesis procedure in bulk as well as thin film form. These samples were characterized for various structural, electrical, optical and magnetic properties. The techniques used for these measurements such as XRD, PES (XPS, UPS), UV-Vis, Z-scan and SQUID-VSM will be discussed following the discussion on preparation techniques.

2.1 Sample preparation

For any experimental research problem good quality samples are must. A well organized methodology for sample preparation is needed. Various techniques are employed for the preparation of samples in bulk and thin film form. These techniques may be classified as physical or chemical. For the preparation of bulk targets we have employed physical method namely solid state reaction route which involves the physical interaction among the reacting species.

2.1.1 Preparation of bulk targets

Solid state reaction method is generally employed for preparation of polycrystalline samples. This method involves the reaction of solid materials at high temperatures as solids generally do not react at room temperature. The various steps which are followed during the sample preparation in solid state reaction route are discussed below;

Step I: In order to ensure the proper mixing of the starting materials or the replacement of dopant in the host matrix, stochiometrically weighted amount of the solid powders are properly mixed and grinded for almost 7-8 hrs continuously.

Step II: In order to ensure the removal of volatile impurities and the inter-diffusion of the solid materials, the powder samples are calcinated at an optimum temperature of 900°C for 24 hrs.

Step III: After calcination the powder samples are again grinded for about 2 hrs properly.

Step IV: In order to ensure the good adhesion and binding of powder molecules the samples are mixed with the poly vinyl alcohol (PVA) binder solution and mixed properly.

Step V: The surface area of reacting solids has a great influence on reaction rates; hence the area of contact between the reactants is increased by pressing the reacting powder into pellets. The powder targets are palletized by applying very high pressure (≈110 kN/cm²). After this the samples are heated at 1400°C. During this process, PVA binder is removed.
and the phase formation of compound takes place.

### 2.1.2 Thin film deposition

Once the single phase crystalline bulk targets are prepared according to above procedure, the next step is to deposit high quality thin film for the prepared target on a properly chosen substrate. Here, first a brief introduction of the thin films will be given followed by the various deposition techniques. After that pulsed laser deposition technique will be discussed in detail.

Thin film is a layer of material on a substrate. A 'thin film' may be arbitrarily defined as a layer of material having at least one dimension varying from a few Å to about 1 μm or so, while other two dimensions are relatively much larger. Thin films are classified as

- Ultra thin film: In this category of films, the thicknesses of the films are ≤ 100 Å.
- Thin film: Thickness ≥ 100 Å and ≤ 5000 Å
- Thick film: Thickness ≥ 5000 Å;

Depending on the thickness of the film their properties change. Properties also depend on grain or microcrystalline size if the film is polycrystalline. During the thin film deposition process, the bulk target is deposited onto a substrate in the form of vapors. The process of thin film deposition comprises of three stages [1].

**Stage I:** Formation of the vapor phase from the condensed phase takes place. Different methods which are used for vapor creation are electron beam evaporation; sputtering, ion deposition, laser ablation and so on.

**Stage II:** In stage II, the transport of atoms or molecules from the source target to the substrate takes place. The vapor species are transported from the source to the substrate with or without collisions among ions, atoms and molecules present in vapor.

**Stage III:** This stage involves the condensation of the vapor species onto the substrate and subsequent formation of the film by nucleation and growth processes.

The degree of independent control of these three steps determines the versatility or flexibility of the deposition process. Two main processes are developed for thin film deposition:

1. Chemical vapor deposition (CVD) processes, which are generally defined as the deposition on a (usually) heated substrate as a result of numerous chemical reactions at the substrate surface.

2. Physical vapor deposition (PVD) processes, which require creation of material vapors (via evaporation, sputtering, or laser ablation) by physical methods and their subsequent condensation onto a substrate to form the film.
The various CVD methods are listed below.

- Low-Pressure CVD (LPCVD)
- Plasma-Enhanced CVD (PECVD)
- Atmosphere-Pressure CVD (APCVD)
- Metal-Organic CVD (MOCVD)

The various PVD techniques are listed above.

- Thermal evaporation
- E-beam evaporation
- Pulsed Laser Deposition PLD
- Reactive PVD
- Sputtering
- Molecular Beam Epitaxy

Since, we have employed PVD process (PLD) for the preparation of thin films so only PLD technique will be discussed in detail here.

2.2 Pulsed laser deposition (PLD)

Pulsed laser deposition (PLD), also called as laser ablation, is a physical vapor deposition technique in which the material to be deposited is irradiated with a series of highly energetic, focused, short laser pulses and the material is evaporated due to increase in surface temperature of the solid target above its melting point. This produces a large number of excited atomic and molecular states in an ablation plume. The whole process occurs in deposition chamber in which the pressure can be adjusted during deposition depending upon the materials requirement. The interaction between the laser and the solid target requires information about the power density, pulse duration and wavelength of the laser as well as target to substrate distance. This interaction is also influenced by properties of the material. One of the most fascinating properties of PLD is that, good stoichiometry can also be achieved. This technique is employed for the growth of wide range of materials such as oxides, superconductors, intermetallics, etc. For the growth
Chapter 2. Synthesis...

2.2. Pulsed laser deposition (PLD)

Figure 2.1: Pulsed laser deposition setup.

of oxides, oxygen gas is supplied into the deposition chamber. By varying the oxygen pressure the oxygen content of the deposited film can be monitored.

For multicomponent inorganics, ablation conditions are chosen such that the ablation plume consists primarily of atomic, diatomic, and other low-mass species. This is typically achieved by selecting an ultraviolet (UV) laser wavelength and nanosecond pulse width that is strongly absorbed by a small volume of the target material. In PLD the main components are a laser source (here 20 ns, 248 nm, excimer laser) and deposition chamber including optical lenses and windows. A brief introduction about the excimer laser is given below:

2.2.1 Excimer laser

Excimers (that is, excited dimers) are molecules that are bound in excited states but are unstable in their electronic ground states [2]. Examples are diatomic molecules composed of closed-shell atoms with $^1S_0$, ground states, such as the rare gases, which form stable dimers He$_2^*$, Ar$_2^*$, etc., but have a mainly repulsive potential in the ground state with a very shallow Vander Waal minimum (Fig. 2.2). The well depth of this minimum is small compared to the thermal energy $k_BT$ at room temperature, which prevents the stable formation of ground-state molecules. Mixed excimers such as KrF or XeNa can be formed from combinations of closed-shell/open-shell atoms (for example, combination of atomic states $^1S+^2S$, $^1S+^2P$, $^1S+^3P$, etc.), which lead to repulsive ground-state potentials. Excimer lasers are also called as RGH (rare gas halogen) and utilize approximately (0.1-0.5)% of halogen donors like F$_2$, 2-5% of a rare gas like Kr and the remaining portion contains buffer gas such as He or Ne. The pressure of the buffer gas is about 2-4 atm., and serves as absorbing the initial excitation energy. Noble gases like (Kr, Xe etc.) in
the excited state have one electron in the outermost shell while as halogens are short of one electron in the last shell. Hence both these (an excited noble gas atom and halogen) combine and form a molecule resulting in the series of energy transfer steps; electron transfer to F to produce negatively charged F ion that combines with a positively charged Kr ion to produce an ion pair in the excited state. In the ground state, the excimer molecule dissociates rapidly with mean life time of 10 fs which is much smaller than the mean life time of excited state (about 5-15 ns). The typical reaction (harpoon reaction) may be
\[
\text{Kr}^+ + \text{F}^- + \text{Kr} \rightarrow (\text{KrF})^* + \text{Kr}
\]
Here Kr acts as a third body in the collision process to remove excess K.E. Laser action is associated with the transition from bound excited state to the dissociative state as shown in fig. 2.2.

Gains in excess of \(10^4\) can be reached for a typical excimer cavity of length 1 m. This allows large gain even when the reflectivity mirrors are not present in the laser system so that laser operation is possible with relative ease. The life time of the laser system is given in terms of number of pulses and is typically in the range of \(10^8\).

### 2.2.2 Advantages of PLD

- This technique enables the stoichiometric transfer of ablated material from multi-cation targets for many materials.

- PLD is compatible with background pressures ranging from ultrahigh vacuum (UHV) to 1 Torr.
Chapter 2. Synthesis...

2.2. Pulsed laser deposition (PLD)

- Epitaxial films of multicomponent inorganics can be formed with effective yield.
- Multilayer and bilayer structures can be prepared in multi-target PLD system.
- PLD is a low-temperature process which is effective for crystalline thin-film formation [3].

Disadvantages

- PLD cannot be used for deposition on large area and lacks in thickness uniformity.
- Particulates can be formed during deposition.
- Depositing wide band gap materials is challenging.

2.2.3 Deposition parameters

Important deposition parameters which govern the quality of film during growth using PLD are,

- Vacuum
- Target to substrate distance.
- Substrate temperature
- Laser parameters, like, energy density, repetition rate, laser wavelength, etc.
- Background gas pressure

Providing thermal energy to the substrate is like providing the energy to the deposited atoms, ions, or molecules. This energy provides sufficient energy to the deposited atoms, ions and/or molecules for nucleation and growth. Too high substrate temperature may result in the diffusion between substrate and film leading to creation of particulates of secondary phase or defects.

The important laser parameter is energy density at the surface of target material. If the energy density is greater than a certain material dependent threshold value, the ejection of particles takes place from the target surface. Also increase in energy density results in the increased amount of ablated material and its kinetic energy. This can also lead to ejection of microglobules from the target material.
Vacuum in the deposition chamber is necessary to make pure films. The background gas is introduced that serves two purposes. First, the formation of multi cation thin-film materials often requires a reactive species (e.g., molecular oxygen for oxides) as a component of the flux. Interaction of ablated species with the background gas often produces molecular species in the ablation plume. Background gas is also used to reduce the kinetic energies of the ablated species of the order of several hundred electron volts down to approximately 1 eV. This is the consequence of the scattering and broadening of the angular distribution of the plume. Due to this the number of ablated particles reaching at substrate placed directly in front of the target is reduced.

2.3 Structural characterizations

In order to have detailed knowledge about the crystal structure and electronic structure of the prepared sample, it is important to characterize them. Accordingly, we have characterized the grown samples first by X-ray diffraction for crystal structural investigations. In order to elucidate the electronic structure, the grown samples were further characterized by X-ray photoelectron spectroscopy and ultraviolet photoelectron spectroscopy. Each technique used for the characterization of the samples will be discussed below.

2.3.1 X-ray diffraction

XRD is one of the most prominent techniques used for addressing all the issues related to crystal structure and phase determination; like lattice parameters, grain size, space group etc. If the wavelength emitted in the form of photons has a value $10^{-2}-10^{2} \text{Å}$, then they are referred to as X-rays corresponding to photon energies in the range of $10^{2}-10^{6} \text{eV}$. For diffraction applications, only short wave length X-rays (wavelength in the vicinity of 1keV) are used. Since the wavelength of X-rays is comparable to the size of inter-atomic distance, they are ideally suited for probing the structural arrangement of atoms and hence provide detailed information about the various structure parameters like lattice parameter, particle size, unit cell volume, etc. X-rays primarily interact with electrons in the atoms. X-ray photons when interact with electrons results in the oscillation of electrons. Due to oscillations, they emit radiations with the frequency of the incident radiation. These are the X-rays that we measure in a diffraction experiment. Diffracted X-ray from different atoms can interfere with each other and the resultant intensity distribution is strongly modulated depending upon the atomic arrangement which causes diffraction of X-rays. If the atomic planes are arranged in a periodic array, the diffracted waves will consist of sharp, interference maxima (peaks) with the same symmetry as
in the distribution of atoms. According to Bragg's law of X-ray diffraction, a certain wavelength of radiation will constructively interfere if they are reflected between crystal planes with a path difference equal to an integral number of wavelengths i.e.

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

Where \( n \) is an integer, \( \lambda \) is the wavelength of X-rays, \( d \) is the inter-planer spacing of planes and \( \theta \) is the angle between the incident ray and the planes of reflection. The schematic view of the XRD measurements is presented in fig. 2.3(a). For performing the XRD measurements, diffractometer has three basic components; (i) The X-ray source (ii) Goniometer, and (iii) X-ray detector.

With monochromatic radiation, an arbitrary setting of a crystalline solid in a beam of X-rays will not in general produce any diffracted beams. Some way of satisfying the Bragg law must be devised, and this can be done by continuously varying either \( \lambda \) or \( \theta \) during the experiment. The commonly used method for XRD measurements is the powder diffraction method which involves the change in \( \theta \) keeping \( \lambda \) fixed. The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle \( \theta \) while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of \( 2\theta \) as shown in fig. 2.3(b). The instrument used to maintain the angle and rotate the sample is termed as Goniometer. In our work, we have used Bruker powder diffractometer for XRD measurements using \( \theta - 2\theta \) geometry in the \( 2\theta \) range \( 20^0 - 80^0 \).

### 2.3.2 X-ray photoelectron spectroscopy

Photoelectron spectroscopy (like X-ray photoelectron spectroscopy, Ultraviolet photoelectron spectroscopy, Auger electron spectroscopy) is a spectroscopic technique involving...
photonics and electrons, mainly used for the investigation of the composition and electronic structure of atoms, molecules, compounds, and surfaces present in a material. In XPS, monochromatic X-ray photons impinge on a sample and, due to the photoelectric effect, electrons are ejected whose energy is measured. The emitted photoelectrons have a kinetic energy distribution consisting of discrete peaks related to the binding energies of the core levels of photoionized atoms. Those electrons which are excited and escape without energy loss contribute to the characteristic peaks in the spectrum; those which undergo inelastic scattering and suffer energy loss contribute to the background of the spectrum. Once a photoelectron has been emitted, the ionized atom must relax in some way. This can be achieved by the emission of an X-ray photon, known as X-ray fluorescence. The other possibility is the ejection of an Auger electron. XPS involves the interaction of X-ray photons with electrons in the energy range 1-5 KeV for soft X-rays, and 5-8 KeV for hard X-rays and is widely used to study the chemical composition and/or speciation of the outer 1-2 nm of the solid surface. XPS is also a sensitive probe of the chemical environment and/or oxidation state of surface species. Core level XPS is highly sensitive to the chemical environment, i.e. the binding energy may be strongly dependent on the oxidation state of the investigated ion, as well as on the neighboring atoms.

X-rays can penetrate micrometers below the surface. By tuning the kinetic energy of photoelectrons to the minimum of their mean free path in the solid, the measurement is sensitive to the topmost atomic layers only. Most of the times an amount of energy is lost which results in the spectral background and the decrease in mean free path of the photoelectron. The main spectral features are observed from the surface region only. The sensitivity of XPS signal is also reduced due to the presence of an adsorbed surface layer of some thickness when the sample is exposed in open atmosphere. One way of reducing the adsorbate surface during the experiment is by Argon sputtering. Photoelectron spectroscopy can be understood as a three step process:

1. Probability of creation of photoelectron by photoexcitation of the solid
2. Transport of photoelectron to sample surface, and
3. Emission of photo emission into vacuum and then to the energy analyzer

Photoelectrons generated by the incident photon energy $h\nu$ are transported to the continuum where they are detected by electron energy analyzer. This is possible only if the incident photon energy is sufficient enough so that it is equal to or greater than;

1. Binding energy ($E_b$) of the electron in a particular atomic orbital (always measured with reference to the Fermi level ($E_F$))
2. Work function ($\Phi_S$) of the sample under investigation

Mathematically we can write $h\nu = E_b + \Phi_S + E_{Kin}$, $E_{Kin}$ being the kinetic energy of the photoelectrons. Since the electron is to be detected by analyzer of work function $\Phi_A$, therefore, the above equation can be modified as $E_{Kin} = h\nu - E_b - \Phi_S - (\Phi_A - \Phi_S)$. This gives

$$E_b = h\nu - \Phi_A + E_{Kin} \hspace{1cm} (2.2)$$

XPS spectrum is recorded at a spectrum of binding (kinetic) energies and has contribution from a background signal and resonance peaks characteristic of the bound states of the electrons in the surface atoms. The resonance peaks above the background are the significant features in an XPS spectrum. Since $\Phi_S$ cancels, the photoelectron energy is known and the $\Phi_A$ is constant, the $E_{Kin}$ determines the $E_b$ and vice versa. For calculating $\phi_A$ (about 4-5 eV) the energy scale is set to zero at the Fermi edge of the reference samples like Ag, or Ni or Au [7]. This calibration results in $\Phi_A$ equal to zero and $E_b$ and $E_{Kin}$ are directly related through $E_{Kin} = h\nu - E_{Kin} - E_b$. It should be kept in mind that this analysis is valid for the conducting samples where the Fermi level is equal for sample and analyzer (see fig 2.4). In the case of insulators or where there is charging effect, the Fermi level is not well defined leading to an energy shift. Two different types of X-ray sources are generally used: MgKα ($h\nu = 1253.6$ eV, line width 0.70 eV) and AlKα ($h\nu = 1486.6$ eV, line width 0.85 eV).

**Spectral feature:** There are generally six features seen in a typical XPS spectrum [5]. These are summed as below:

1. **Sharp peaks** due to photoelectrons created within the first few atomic layers (elastically scattered). These peaks constitute the main spectral feature which
correspond to the particular element of interest.

2. **Background**: A broad structure due to electrons from deeper in the solid which are inelastically scattered (reduced K.E) forms the background. In the measured spectrum it can be found that in addition to the primary spectrum, which is the combination of the main line and intrinsic excitation, there is also the secondary spectrum representing the inelastic events after the photoexcited electron has left the site of the excitation process. Most often secondary spectrum constitutes the background on the high binding energy (low kinetic energy) side of the main elemental peak [6].

3. **Multiplet splitting**. Multiplet splitting occurs when there are unfilled shells containing unpaired electrons. For instance, transition metals with unfilled p and d orbitals and rare earths with unfilled f orbitals all show multiplet splitting. This splitting arises from exchange interactions between the odd number of electrons in the core level from which electron emission took place and any unpaired valence electrons.

4. **Satellites** are due to a sudden change in Coulombic potential as the photo ejected electron passes through the valence band. Satellites arise when a core electron is removed by a photoionization. There is a sudden change in the effective charge due to the loss of shielding electrons. (This perturbation induces a transition in which an electron from a bonding orbital can be transferred to an anti-bonding orbital simultaneously with core ionization). Two types of satellite features are detected.

   **Shake-up satellites**: These are observed when the outgoing electron interacts with a valence electron and excites it (shakes it up) to a higher energy level. As a consequence the energy of emitted core electron is reduced and a satellite structure appears a few eV below (KE scale) the core level position. If the valence electron is ejected from the ion completely to the continuum, the **Shake-off** satellites are observed. These satellite features appear as a broadening of the core level peak or contribute to the inelastic background.

5. **Plasmons**; It is created by collective excitations of the valence band electrons and is observed above the background and are typically of the order of 10-20 eV. At the first plasmon peak, a slight hump indicates the surface plasmon of which the loss energy is about \( \frac{1}{\sqrt{2}} \) times that of the usually more intense-bulk plasmon [7].

   - **Extrinsic plasmon**: It appears due to the excitations produced when the energetic photoelectron propagates through the solid after the photoelectric process.
• **Intrinsic plasmon**: Present due to the screening response of the solid to the sudden creation of the core hole in one of its atom. The two kinds of plasmon are indistinguishable.

6. **Auger peaks**: Photoelectron emission is sometimes accompanied by Auger electron emission since this represents the primary route for the dissipation of energy introduced by core hole production. These are produced by x-rays (transitions from L to K shell: $O_{KLL}$ or $C_{KLL}$).

**Instrumentation of XPS**

A typical XPS experimental station/instrument primarily consists of

1. The specimen on a sample holder with x-y-z movement stage
2. An X-ray source
3. Extraction optics and energy filter
4. Hemispherical energy analyzer
5. An auxiliary ion gun

In the present study, X-ray Photoemission Spectroscopy measurements were carried out using AIPES beamline of UGC DAE CSR, Indore at INDUS I, RRCAT, Indore which is equipped with AlK$_\alpha$ and MgK$_\alpha$ lab source. The experimental setup at INDUS-I is shown in fig. 2.5.

![Figure 2.5: Experimental workstation of AIPES beamline at Indus -1 RRCAT, Indore, India.](image-url)
2.3.3 Ultraviolet photoelectron spectroscopy

Ultra-violet photoelectron spectroscopy (UPS) also called as valence band spectroscopy (VBS) is based on the same working principle except the energy range of photons ($50 \text{ eV} < h\nu < 200 \text{ eV}$) used for excitation. In UPS, low energy photons (generally in the region vacuum ultraviolet) are used which can probe the valence band structure of the solid material, hence the name as VBS. In UPS He-I (21.2 eV) and He-II (40.8 eV) are also used as lab source. Now-a-days availability of synchrotron radiation (SR) sources having unique features like (a) the extremely high brightness of the excitation and (b) the tunable photon energy have made it possible to do the in depth studies by using varied photon energies, so that one can study the energy dependent UPS. The main difference between laboratory radiation source and SR source is that the photon energy in case of SR can be selected by use of a monochromator from a continuous spectrum over a wide range. SR sources bridge the traditional gap between XPS and UPS where the distinction was based on source used. UPS enables to study the valence levels including some outer most d- levels of the transition metals ions. Photoemission spectroscopy is performed in two different modes, viz; angle integrated (AIPES) where electrons emitted are collected over a wide solid angle of emission, and angle resolved photoemission (ARPES) spectroscopy in which the photoelectrons and incident photon beam are in a specific direction. AIPES enables to study the density of states in polycrystalline solids, while ARPES is generally used to investigate the Fermi surface topologies of single crystals.

To fulfill the two basic requirements (1) good photon flux and (ii) moderate resolution for carrying out photoemission experiments, reflection mirrors and monochromators with surfaces of spherical, toroidal, cylindrical, ellipsoidal or parabolic shape are often employed for a wide $h\nu$ region in addition to bent crystals for X-rays. In either case, the materials of the gratings or crystals should withstand the strong radiation without suffering from possible radiation damage. When the heat load onto these optical components is quite high, indirect cooling by water or liquid nitrogen is employed [8]. Platinum coated pre and post - mirrors of toroidal type and toroidal grating monochromators (TGM) with three different gratings at 200, 600 and 1800 lines/mm are placed in AIPES beamline at RRCAT Indore.

Data Collection in photoelectron spectroscopy experiment

X-ray photoelectron (XP) spectra provide the binding energies of electrons detected, measured in electron-volts (eV). Detectors have accuracies on the order of $\pm 0.1 \text{ eV}$. The binding energies are used to identify the elements to which the peaks correspond. XPS data is given in a plot of intensity versus binding energy. Intensity may be measured
in counts per unit time (such as counts per second, denoted c/s). Often, intensity is reported as arbitrary units (arb. units), since only relative intensities provide relevant information. Comparing the areas under the peaks give relative percentages of the elements detected in the sample. Prior to the measurement the sample is cleaned with Ar ions for reducing the contamination due to exposure to atmosphere. Initially, a survey photoelectron spectrum is obtained, which shows all of the detectable elements present in the sample. Elements with low detection or with abundances near the detection limit of the spectrometer may be missed with the survey scan. Subsequently, high resolution scans of the peaks can be obtained to give more information. Elements of the same kind in different states and environments have slightly different characteristic binding energies. A computerized mathematical model is used to fit peaks within the elemental peak which represent different states of the same element, commonly called deconvolution of the elemental peak. These peaks are deconvoluted, which provide the information related to the core level binding energies, charge state, etc.

2.4 Optical measurements

Optical measurements of a material can be performed by recording the interaction between electromagnetic radiation and the material. The properties which can be studied by performing optical measurements include absorption, diffraction, polarization, reflection, refraction, and scattering effects. Optical measurements are performed for the investigation of molecular, atomic, and electronic processes. Optical properties of semiconductors give information about the nature of their electronic band structures which are in turn related to the type of crystallographic structure, the particular atoms, and their bonding. In semiconductors (doped and undoped) both valence-band states and conduction-band states take part in optically induced transitions. In order to explore the electronic processes in semiconductors and related materials, electronic transitions play an important role. For this purpose optical measurements in the range of Ultra Violet-visible spectroscopy is an important tool. The energy range (1eV-10eV) of UV-Vis spectroscopy corresponds to the transition energy between valence band states to conduction band states.

In the present thesis, UV-Visible spectroscopy is employed to calculate the optical absorption, transmission and also energy band gap values. A brief discussion about the UV-Vis spectroscopy is given in section 2.4.1. We have also measured the nonlinear optical refraction and nonlinear absorption coefficients using Z-scan technique which will be discussed in section 2.4.2.
2.4.1 Ultraviolet-visible spectroscopy

Ultraviolet-visible spectroscopy (UV-Vis or UV/Vis) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region (200-800 nm). This means it uses light in the visible and adjacent (near-UV and near-infrared (NIR)) ranges. In this region of the electromagnetic spectrum, molecules undergo electronic transitions (promotion of electrons from the ground state to a high energy state).

Energy absorption is most typically associated with electronic transitions involving bonding orbitals, for the most part, those containing s + p electrons. During the interaction of UV-Vis radiation with materials, the following electronic transitions are possible:

1. $\pi - \pi^*$ (pi to pi* transition)
2. $n - \pi^*$ (n to pi* transition)
3. $\sigma - \sigma^*$ (sigma to sigma* transition)
4. $n - \sigma^*$ (n to sigma*)

The transitions are shown in the hypothetical energy diagram in fig. 2.6. The uninvolved n (non-bonding) electrons have no antibonding orbital. The $\sigma - \sigma^*$ transition requires an absorption of a photon with a wavelength which does not fall in the UV-Vis range. Thus, only $\pi - \pi^*$ and $n - \pi^*$ transitions occur in the UV-vis region. From the fig. 2.6 it can be seen that $\sigma - \sigma^*$ and $n - \sigma^*$ transitions require relatively high energy and are therefore associated with shorter wavelength radiation (ultraviolet). The relationship between the particular electronic transition (electronic energy) and the wavelength that stimulates this transition is called as specific absorption and the plot of these points along the wavelength scale at which a given substance shows absorption peaks or maxima is called an absorption spectrum.

![Energy level diagram](image)

Figure 2.6: An energy level diagram of the possible transitions involved in UV-Visible spectroscopy. Cross mark shows the forbidden transitions.
The absorption of light is directly proportional to both the concentration of the absorbing medium and the thickness of the medium in the light path. A combination of the two laws (known jointly as the Beer-Lambert Law) defines the relationship between absorbance (A) and transmittance (T).

\[ A = \log I_0 / I = \log 100 / T = \epsilon c b \]  

where A is absorbance (no unit of measurement), \( \epsilon \) is molar absorptivity (dm\(^3\)mol\(^{-1}\)cm\(^{-1}\)), c is molar concentration (mol dm\(^{-3}\)), and b is path length (cm). It is important to note that \( \epsilon \) is a function of wavelength and so the Beer-Lambert law is true only for light of a single wavelength, or monochromatic light. The absorption coefficient and the band gap energy can be described by the following equation

\[ \alpha h\nu = A(h\nu - E_g)^{1/2} \]  

where \( \nu \) is the incident photon energy, \( E_g \) is the band gap energy and A is a constant. A plot of \( (\alpha h\nu)^2 \) versus \( h\nu \) is made to determine \( E_g \) using the linear fit process. The band gap can be calculated by using the simple relation between the wavelength and the energy of the incident photon. \( h\nu / c = E_g = 1237.5 / \lambda (eV) \), \( \lambda \) is the wavelength at which the absorption edge is observed. \( c \) is the speed of incident photon and \( h \) is Planck's constant.

2.4.2 Z-scan technique

Z-scan is one of the simplest and standard technique for separately determining the nonlinear changes in absorption and refraction. Accurate determination depends on how precisely the laser source is characterized in terms of its temporal and spatial profiles, (any change of beam profile within the nonlinear sample). Changes in the refractive index due to optical nonlinearities in the sample are detected as characteristic intensity variations of the transmitted signal as a function of the sample position. This technique is based on the principle of spatial beam distortion [9]. In this technique, the sample is moved in the z-direction along the axis of the tightly focused Gaussian laser beam and the field intensity is measured as a function of sample position. While the input energy is kept constant, the sample experiences different incident field values at different z-positions. To examine the intensity dependence of nonlinear absorption and nonlinear refraction, open aperture (OA) and closed aperture (CA) Z-scan experiments are carried out [9]. In the OA Z-scan experiment, a convex lens is used to collect all the transmitted light at the detector and the detector is placed at the focal plane of the lens, while in closed aperture, only the on-axis beam is allowed to enter the detector.
The OA Z-scan enables one to determine nonlinear absorption coefficient ($a_2$). CA Z-scan method is the efficient technique for determining both the magnitude as well as sign of the nonlinear refractive index $n_2$. In this geometry, the normalized transmittance of the sample exhibits a pre-focal transmittance maxima (peak) followed by a post-focal minima (valley). The appearance of peak followed by valley is the signature of positive $n_2$ while the opposite feature indicates a negative $n_2$. Before performing the measurement on a particular interest it is necessary to take care of some issues as listed below.

1. The thickness of the sample should be smaller than $z_R$ (Rayleigh range) so that the film experiences uniform intensity throughout its thickness.

2. The film area should be sufficiently large as compared to the spot size of the incident laser beam which enables to neglect the probable diffraction errors in the experiment.

3. The contributions from the substrate (in case of thin film samples) to the calculated parameters should be negligible.

2.5 Transport and magnetotransport measurements

The word transport here refers to the motion of charge carriers in the presence of external electric filed. Magnetotransport defines the charge transport under the influence of both electric and magnetic field. In both the cases, the motion of charge carriers is affected due to different scattering mechanisms, like scattering by other carriers, lattice, grain boundaries, etc. This scattering results in the opposition to the flow of current which is called as resistivity. Measuring the resistance or resistivity of a semiconductor is very important as it contributes to the device series resistance, capacitance, threshold voltage, and other parameters. The resistivity depends on the free electron and hole densities $n$ and $p$, and the electron and hole mobilities $\mu_n$ and $\mu_p$ as well.

During transport of the charge carriers in any material, if external magnetic field is applied, the carriers interact with the magnetic field also. This interaction also results in the change in resistance. The relative change of the resistance due to the presence of magnetic field is called as magnetoresistance (MR). Magnetoresistanc is an important tool to study the behavior of charge carriers under the influence of magnetic field. Here in this part of chapter, the basic technique for the measurement of resistivity and magnetoresistance will be discussed. Hall measurement technique will be also discussed followed by the current voltage measurements.
2.5.1 Resistivity and magnetoresistance measurements

Electrical resistivity $\rho$ of a sample can be calculated using equation,

$$\rho = R(A/l)$$  \hspace{1cm} (2.5)

where, $R$ is the resistance of the sample, $l$ is the distance between the contacts and $A$ is the cross-sectional area of the sample.

Two-point probe method is the simplest method used for measuring resistance and appear to be easier to implement as only two probes need to be manipulated (fig. 2.7(a)). In two probe technique an unwanted contact resistance arises which prevents from measuring the accurate resistance. The voltage drop in two probe technique is given by

$$V = V_{\text{sample}} + 2V_{\text{lead}} = IR_s + 2IR_L$$  \hspace{1cm} (2.6)

here the factor 2 in second term of R.H.S is due to contribution of connecting leads of the voltage source. $R_S$ and $R_L$ correspond to the sample resistance and lead resistance, respectively. The error which is always linked due to the presence of lead resistance with the measurement is $\sim 2R_L/R_S$.

![Schematics of (a) two probe and (b) four probe technique for determining the resistance of the materials.](image)

Four-point probe technique is commonly used to measure the resistivity of the semiconductor. In four probe technique, the probes are generally collinear, i.e., arranged in-line with equal probe spacing, but other probe configurations are possible [10]. In four probe technique the current and voltage are supplied through separate probes. Current is passed through outer two probes and the voltage drop is measured across inner two probes. The arrangement is shown in fig. 2.7(b). As the voltage measuring device draws negligible current in this arrangement, so this technique has advantage of removing the errors arising due to contact resistance. Here the voltage drop is given by

$$V = V_{\text{sample}} + 2V_{\text{lead}} = IR_s$$  \hspace{1cm} (2.7)
Since no current is drawn through voltage measuring loop (fig. 2.7(b)), hence the second term of the R.H.S, $V_{lead}$ becomes zero. So in four probe technique, very small resistance with great accuracy can be measured.

For MR measurements, resistance is measured in both presence $\{R(H)\}$ as well as absence $\{R(0)\}$ of external magnetic field $\{H\}$. Measuring resistance by four probe technique in the presence of (varying) magnetic field will give the magnetoresistance (MR) (in %age) and is defined as:

$$\frac{\Delta \rho}{\rho} (\%) = \left( \frac{R(H) - R(0)}{R(0)} \right) \times 100$$  \hspace{1cm} (2.8)

where, $\Delta \rho$ is the change in resistance/resistivity due to magnetic field. The direction of magnetic field can be varied with respect to the direction of flow of current. Accordingly we can measure longitudinal MR; when the direction of current is parallel to magnetic field and, transverse MR; when the direction of current is perpendicular to direction of magnetic field. One can also measure the magnetoresistance of the same sample in both longitudinal and transverse configuration by changing the direction of current and/or magnetic field during the measurement. This is called as anisotropic MR.

In the present thesis, we have measured both resistivity (conductivity) and MR using linear four-probe technique. Temperature dependent DC resistivity (conductivity) of the grown samples are measured at 0T. Longitudinal MR measurements are carried out in varying magnetic field (0 T-8 T) and temperature (2 K-300 K). A superconducting magnet cryostat, Oxford instruments, has been employed to carry out the measurements at UGC-DAE CSR, Indore.

### 2.5.2 Hall measurements

The resistivity is related to the carrier density. Hall measurements are widely used for the calculation of carrier density, the carrier type, and the mobility density. For performing the Hall measurements, a sample of well defined shape (generally rectangular) is placed in crossed electric (E) and magnetic (B) fields. This results in the action of Lorentz force on the mobile charge carriers which finally gives the Hall voltage ($V_H$) perpendicular to both E and B.

The Hall coefficient ($R_H$) is determined experimentally as:

$$R_H = \frac{t V_H}{B I}$$  \hspace{1cm} (2.9)

where $t$ is the sample thickness, $B$ the magnetic field, and $I$ the current. For the calculation
of carrier density in extrinsic p-type material with $p > n$, $R_H$ is given by

$$R_H = \frac{1}{qp}$$

(2.10)

and for extrinsic n-type it becomes,

$$R_H = -\frac{1}{qp}$$

(2.11)

here, $q$ represents the charge of carrier, and $p$ and $n$ refers to the density of holes and electrons, respectively. From above relation one can calculate the hole and electron density in p- and n-type semiconductor.

In the present thesis, the effect of temperature on the charge carrier is investigated by carrying out the Hall effect measurements in 9 T ACT PPMS, system from Quantum Design, USA.

### 2.5.3 Current-voltage measurements

Current-voltage measurements are performed for the investigation of transport and charge distribution and getting general information on the material. The electrical signal of the semiconductor is collected via Ohmic or Schottky contacts, depending on the parameters to evaluate [11]. It is important to have good performance of electrical contacts like, Ohmic conduction analysis is useful for determining the model of charge carrier transport and in some cases to observe the role of shallow levels [12]. To investigate how the semiconductor device behaves at different values of current and voltage, current-voltage measurements are performed. These measurements also provide the insight about the bipolar conduction process in semiconductors.

In the present thesis I-V measurements are performed at cryogenic temperatures (2 K-300 K) in linear four-probe geometry using superconducting magnet cryostat, Oxford instruments at MTCL lab., UGC-DAE CSR, Indore.

### 2.6 Magnetization measurements

Semiconductors when doped with magnetic impurities (Diluted magnetic semiconductors) exhibit magnetism. In order to have a clear understanding of magnetic ordering in the sample, it is important to know the way in which magnetic properties are measured. For the experimental study of magnetic materials, one requires (a) a means of producing the
field which will magnetize the material, and (b) a means of measuring the resulting effect on the material. Superconducting quantum interference device (SQUID) magnetometer

Figure 2.8: SQUID (superconducting quantum interference device) flux sensor. Schematic view of a commercial SQUID magnetometer consisting of a liquidHe cryostat, a superconducting magnet, the variable-temperature sample chamber with thermometers and the detection coils close to the sample position. (Reproduced from [13])

is one of the most sensitive devices. It can be used for measuring very small magnetic fields $\sim h/2e = 2.07 \times 10^{-15}$ weber or Tm$^2$, or $2.07 \times 10^{-7}$ Maxwell or Gauss cm$^2$ with high resolution [14]. This device is based on the tunneling of superconducting electrons across a very narrow insulating gap, called a Josephson junction, between two superconductors. In this device, a current flows through a superconducting ring in such a way that the current is equally distributed through two Josephson junctions, as shown in fig. 2.8(a). The linear periodic motion of the sample with a vibration frequency of 0.15 Hz causes a change of magnetic flux through the ring. This in turn adds a current in one junction, and subtracts in the other. The whole phenomena leads to periodic appearance of voltage between two different and opposite points (A and B) as shown in fig. 2.8(a). Each voltage step corresponds to the passage of a single flux quantum across the boundary of the ring. A SQUID magnetometer is usually combined with a superconducting magnet and a variable-temperature He cryostat, which allows for measurements in high fields (upto 7 T for commercial instruments) and at low temperatures. Fig. 2.8(b) shows the schematic view of commercial SQUID magnetometer.

In the present thesis we have performed temperature dependent magnetization measurements using Quantum Design SQUID-VSM at 500 Oe magnetic field.
References


