Chapter 2

Experimental and analytical techniques

Abstract
Various techniques have been used for the synthesis of the bulk delafossite materials. Silver delafossite requires the synthesis through a low temperature route. Hydrothermal or ion exchange technique has been used for the synthesis of silver delafossites. This chapter describes the preparation techniques of bulk materials and the pulsed laser deposition technique and rf magnetron sputtering utilized for the growth of thin films. A brief description of various analytical tools used for the structural, compositional, electrical and optical properties of the films as well as bulk materials is also included.
2.1 Introduction

The growth techniques play an important role in determining the characteristics of crystals, bulk powders as well as thin films. It has been observed that various physical constants, characteristic to a bulk material, may not be reproduced as the same in their corresponding thin films. The structural, electrical and optical properties of thin films are found to be highly sensitive to the techniques adopted, the substrates chosen, deposition conditions, the presence of defects and impurities and the film thickness. The appropriate choice of an experimental technique thereby helps in tailoring a material with controlled, reproducible and well defined properties so as to suit a technological application. For example the AgCoO$_2$ thin films grown by pulsed laser deposition were amorphous where as highly oriented growth has been achieved by growing the films by rf magnetron sputtering.

The present work is primarily related to studies on new p-type delafossite oxides. Though many reports on the synthesis of copper delafossite exist in literature, synthesis of p-type silver delafossites is sparingly few. The silver delafossites cannot be grown by the high temperature solid state reaction because the decomposition temperatures of these compounds are low. These factors make the synthesis of silver delafossites some what tricky. In the present work the copper delafossites were synthesized by the high temperature solid state reaction. For the synthesis of silver delafossite oxides, two methods viz., hydrothermal synthesis and ion exchange reaction were successfully used. The ABO$_2$ wide band gap delafossite oxides thus synthesized in the laboratory were used for the deposition of thin films. Deposition techniques such as pulsed laser deposition (PLD) and radio frequency (rf) magnetron sputtering were employed.
for the growth of these oxide thin films. Thermally evaporated metal electrodes (aluminum, indium) were used to make contacts for electrical characterisation of the films and pn junctions. The present chapter describes the various methodologies especially the hydrothermal and ion exchange reaction adopted for bulk synthesis and thin film growth. It also briefs on the different analytical tools used in the present study.

2.2 Bulk synthesis

The polycrystalline materials in the powder form were synthesised mainly by three techniques, viz., solid state reaction, ion exchange reaction and hydrothermal synthesis. The powders thus synthesised were sintered at high temperature to make targets for growth of thin films by PLD and sputtering techniques.

2.2.1 Solid state reaction

For preparing bulk p-type delafossite powders, and some of the starting precursors for ion exchange reactions, stoichiometric quantities of the oxides of the starting materials were thoroughly mixed in alcohol medium using an agate mortar and pestle. The dried mixture was then placed in an alumina boat and introduced into the hot temperature zone of a horizontal tube furnace equipped with a proportional integral differential (PID) controller. The firing was done at the requisite temperature over a fixed time. All the oxides were preheated to 300°C before weighing which ensures the powders to be dry. A two step firing process is usually adopted for pellet synthesis. The constituent materials, after thorough mixing, are calcined to complete the reaction and compound
formation. These powders are then pressed into pellets and then sintered at higher temperature.

A solid and highly condensed pellet with reduced porosity is desirable for pulsed laser deposition to arrest cracking due to high thermal conductivity on exposure to the high energy laser. A large press loading can reduce porosity in the target but overloading during pressing results in a cracked target. The pore density can be measured from the following relation,

\[ \text{Pore density} = \frac{\text{Actual mass density}}{\text{Theoretical mass density}} \]

where,

\[ \text{Actual mass density} = \frac{\text{Target weight}}{\text{Target Volume}} \]
\[ \text{Theoretical mass density} = \frac{\text{Weight of all atoms in the primary cell}}{\text{Volume of the primary cell}} \]

2.2.2 Ion Exchange reaction

Inorganic reactions can be divided into roughly three types:

1) Ion Exchange Reactions: Ion exchange is a reversible chemical reaction wherein an ion (an atom or molecule that has lost or gained an electron and thus acquired an electrical charge) from solution is exchanged for a similarly charged ion attached to an immobile solid particle.

2) Redox Reactions: These are characterised by changes in oxidation state of elements

3) Reactions involving complex ions

Ion Exchange Reactions

For an ion exchange reaction: \( \text{AB(aq)} + \text{CD(aq)} \rightarrow \text{AD} + \text{CB} \) to occur, the products cannot both be soluble (ie. a strong electrolyte). One of the products must be one of the following as described in the following examples
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1. An insoluble compound $\text{AgNO}_3(\text{aq}) + \text{NaCl (aq)} \rightarrow \text{AgCl (s)} + \text{NaNO}_3(\text{aq})$ 
   AgCl is insoluble and so forms a precipitate.

2. A weak electrolyte $\text{HCl (aq)} + \text{NaOH (aq)} \rightarrow \text{H}_2\text{O (l)} + \text{NaCl (aq)}$: No precipitate is formed here.

3. A compound that dissociates to form a gas $\text{Na}_2\text{CO}_3(\text{aq}) + 2 \text{HCl (aq)} \rightarrow 2\text{NaCl (aq)} + \text{H}_2\text{O} + \text{CO}_2(\text{g})$ In this reaction, the following has occurred:

   $\text{Na}_2\text{CO}_3(\text{aq}) + 2 \text{HCl (aq)} \rightarrow 2\text{NaCl (aq)} + \text{H}_2\text{CO}_3(\text{aq})$ The $\text{H}_2\text{CO}_3$ immediately decomposes to $\text{H}_2\text{CO}_3(\text{aq}) \rightarrow \text{H}_2\text{O} + \text{CO}_2(\text{aq}) \rightarrow \text{H}_2\text{O} + \text{CO}_2(\text{g})$

   Ion exchange reactions are also called double displacement reactions. An example of an ion exchange reaction is

   $\text{AgNO}_3(\text{aq}) + \text{NaCl (aq)} \rightarrow \text{AgCl (s)} + \text{NaNO}_3(\text{aq})$

   When $\text{AgNO}_3$ and $\text{NaCl}$ dissolve in water, they dissociate completely to their component ions

   $\text{AgNO}_3(\text{aq}) \rightarrow \text{Ag}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$

   $\text{NaCl(}aq\text{)} \rightarrow \text{Na}^-(\text{aq}) + \text{Cl}^-(\text{aq})$

   In the reaction it can easily be seen that it is a double displacement reaction since both the cations ($\text{Ag}^+$ and $\text{Na}^+$) and the anions ($\text{NO}_3^-$ and $\text{Cl}^-$) exchange. As the $\text{Ag}^+$ and $\text{Cl}^-$ ions meet, they react to form insoluble $\text{AgCl}$ which we observe as a precipitate.
If we re-write the reaction equation in terms of the ions that are present, we obtain:

$$\text{Ag}^+(aq) + \text{NO}_3^-(aq) + \text{Na}^+(aq) + \text{Cl}^-(aq) \rightarrow \text{AgCl}(s) + \text{Na}^+(aq) + \text{NO}_3^-(aq)$$

Both $\text{Na}^+$ and $\text{NO}_3^-$ remain unchanged through the reaction and so are called spectator ions. If we exclude these ions from the reaction equation we obtain the net ionic equation:

$$\text{Ag}^+(aq) + \text{Cl}^-(aq) \rightarrow \text{AgCl}(s)$$

**How one make sure there is an ion exchange reaction?**

In an ion exchange reaction, the cations and anions inter change as in this typical example

$$\text{AgNO}_3(aq) + \text{NaCl} (aq) \rightarrow \text{AgCl} (s) + \text{NaNO}_3(aq)$$

So $\text{Ag}^+$ will react with $\text{Cl}^-$ and $\text{Na}^+$ will react with $\text{NO}_3^-$:

$$\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}$$

$$\text{Na}^+ + \text{NO}_3^- \rightarrow \text{NaNO}_3$$

Then check if AgCl or NaNO$_3$ are soluble. If they are, then the ions will remain in solution and there will be no reaction. Silver Chloride, AgCl, is insoluble and so there is an ion exchange reaction.
In the present work the AgGaO\textsubscript{2} bulk powder has been synthesized through ion exchange reaction. AgGaO\textsubscript{2} has two polymorphs $\alpha$-AgGaO\textsubscript{2} and $\beta$-AgGaO\textsubscript{2}.

2.2.3 Hydrothermal synthesis

The term ‘hydrothermal’ is purely of geological origin. Hydrothermal processing can be defined as any heterogeneous reaction in the presence of aqueous solvents or mineralizers under high pressure and temperature conditions to dissolve and recrystallize (recover) materials that are relatively insoluble under ordinary conditions. Recently, Byrappa and Yoshimura have defined hydrothermal [1] as any heterogeneous chemical reaction in the presence of a solvent (whether aqueous or non-aqueous) above the room temperature and at a pressure greater than 1 atm in a closed system. Hydrothermal method is a non-conventional method to obtain nanocrystalline inorganic materials. High temperature, high pressure apparatus called ‘auto-claves’ or ‘bombs’ are needed for hydrothermal synthesis. For hydrothermal experiments, the requirements for starting materials are (1) accurately known composition, (2) as homogeneous as possible, (3) as pure as possible and (4) as fine as possible, etc.

Generally the method is claimed as solvothermal, which means that water, and other solvents are also used in accordance with the general process principle. Polar solvents or even non-polar solvents can be used for the dissolution-recrystallisation process. These solvents have specific disadvantages concerning mainly their toxicity and corrosion problems for the autoclave materials.

The major advantages of processing the materials by hydrothermal method over other methods for powder preparations are 1) materials are formed directly from solution 2) materials can be obtained as anhydrous, crystalline or
amorphous. 3) It is possible to control the particle size and shape by varying hydrothermal temperature. 4) Chemical composition, stoichiometry, etc can be controlled by processing parameters. 5) Powders obtained by hydrothermal technique are highly reactive in sintering and in many cases, powders do not need calcination and milling process.

The grain size of the powders synthesized by hydrothermal method is less than 1 μm. We can make composites like organic/ inorganic mixtures and materials which have very high vapor pressure by hydrothermal method. Both physical and chemical parameters are effective during hydrothermal processing in such a way that direct precursor - product correlation can be established. Temperature, pressure and time of reaction are the three physical parameters in the hydrothermal synthesis. Temperature plays an important role in the kinetics of product formation as well as on the thermodynamic stability of the product phase. Pressure is essential for solubility, the supersaturation range directing to the crystallization process as well as for the thermodynamic stability of the product phase. Time is also an important parameter because the synthesis of kinetically stable phases are favored in short term processes while thermodynamically stable phases are formed in long term experiments, corresponding to a suitable temperature and pressure. The fundamental roles of temperature, pressure, precursors, and time on crystallization kinetics of various compounds are defined empirically [1].

At a given hydrothermal temperature and pressure suitable for the synthesis, the precursor materials are continuously dissolved in hydrothermal fluid. The formation of gels is not observed at any time during the process. Bigger molecular units are hydrolyzed at elevated temperature and pressure.
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In the hydrothermal synthesis, the precursor materials are taken in a container with solid to water proportions of about 1:10. The closed containers are placed into the sealed stainless steel autoclaves and put into the furnace. Applying the desired hydrothermal synthesis temperature, an autogenous pressure is formed. The external pressure is adjusted as soon as the temperature equilibrium is achieved within the autoclave. By the installation of the hydrothermal pressure, the reaction process takes place. Temperature fluctuations of the furnace have negative consequences because a rise in the temperature leads to a higher dissolution rate disturbing the dynamic equilibrium of dissolution-crystallization, while lowering of temperature leads to higher supersaturation.

A key limitation to the conventional hydrothermal method has been the need for time consuming empirical trial and error methods as a means for process development. Material processing under hydrothermal conditions requires a pressure vessel capable of containing a highly corrosive solvent at high temperature and pressure. Ideal hydrothermal apparatus popularly known as an autoclave should have the following characteristics:

i) Inertness to acids, bases and oxidizing agents.
ii) Ease of assembly and disassembly.
iii) Sufficient length to obtain a desired temperature gradient.
iv) Leak-proof with unlimited capabilities to the required temperature and pressure.
v) Rugged enough to bear high pressure and temperature experiments for long periods with no damage so that no machining or treatment is needed after each experimental run.
The Parr bomb used in the present study is a home made teflon lined stainless steel bomb. Since the lining used is teflon the reaction temperate is limited to less than 300°C. For higher temperature a platinum lining is advisable.

2.3 Thin film growth techniques

A ‘thin film’ has one of its linear dimensions very small compared to the other two and is characterised by a large surface to volume ratio. Any thin film deposition process involves the following sequential steps:

1) Transition of the condensed phase (solid or liquid) into the gaseous state (atomic/molecular/ionic species)
2) Transport of the vapor from the source to the substrate
3) Condensation of the vapor upon arrival on the substrate
The deposition techniques are broadly classified into two - physical and chemical - depending on how the atoms/molecules/ions/clusters of species are created for condensation process [2].

Various chemical methods have been realized for thin film deposition of phosphor materials. Some of them are sol-gel synthesis [3,4], solvent evaporation epitaxy method [5], electrophoresis [6], spray pyrolysis [7,7] and dip-coating [9]. Thermal and electron beam evaporation, pulsed ion beam evaporation [10], chemical vapor deposition (CVD) [11], PLD, rf sputtering, and atomic layer epitaxy (ALE) fall under the stream of physical methods, generally adopted for thin film phosphor growth.

The following sections give a brief outline of the various thin film deposition techniques used in the present work.

2.3.1 Thermal evaporation by resistive heating

Thermal evaporation is a simple and convenient technique widely used for the deposition of thin films of metals, alloys and many compounds. The process, in general, involves heating up of a source material until it evaporates and condenses on a cold target surface, referred to as the substrate. If carried out in vacuum, the evaporation temperature can be considerably lowered and the formation of oxides and incorporation of impurities in the growing layer can be avoided. Moreover, at pressures as low as $10^{-6}$ or $10^{-5}$ Torr, the mean free path of vapor atoms shall be of the same order as the vacuum chamber dimensions. Hence, the particles can travel in straight lines from the evaporation source towards the substrate without being significantly scattered [12].

In thermal evaporation technique, the average energy of vapor atoms reaching the substrate surface is generally low (of the order of $kT$ ie. less than...
tens of eV). Here, a refractory metal (tungsten or tantalum) strip or shaped filaments are heated directly by attaching the ends to a low voltage, high current supply to evaporate the charge. The characteristics and quality of the deposited film shall depend on the substrate temperature, rate of deposition, substrate to target distance, base pressure, etc. The homogeneity of the film depends on the geometry of the evaporation source and the distance from the source material to the substrate. Excellent and detailed reviews on the know-how of the technique have been discussed by Holland [13].

In the present work, the deposition of metal electrodes (In) was done using thermal evaporation via resistive heating.

2.3.2 Sputtering

Sputtering is one of the most versatile techniques used for the deposition of high quality thin films over a larger area with better control of composition and thickness, greater adhesion and homogeneity. The process involves the creation of inert gas plasma, usually of argon [14], by applying a high voltage between electrodes. The target holder is generally taken as the cathode and the substrate holder as the anode. The source material is subjected to intense bombardment by heavy argon ions. By momentum transfer, particles are knocked out from the target surface and they travel across the system to condense onto the substrate surface. The process, if carried out in vacuum, becomes more efficient since the sputtered material will arrive at the substrate surface without suffering collisions with the residual gas with energy enough to produce a fine coating. Sputtering is normally performed at a pressure of $10^{-2}$ to $10^{-3}$ Torr. At such high residual gas pressures, the sputtered material is seldom transferred towards the
substrate without many collisions. This gives rise to very slow deposition rate and poor quality coating.

Sputtering may be carried out in a variety of systems, which may differ in sputtering configuration, geometry, target type etc. Experimental sputtering systems usually have small targets and low production rates, whereas commercial production systems have large targets and rapid substrate transport to maximize production rate. Irrespective of the sputtering system used, the basic sputtering process remains the same. A schematic diagram of the rf sputtering system used in the present study is shown in figure 2.2.

Figure 2. 2. Schematic of rf sputter deposition system used for film deposition.

Normally there are two modes of powering the sputtering system - dc and rf biasing. In dc sputtering, a direct voltage is applied between the cathode and the anode. This method is restricted for conducting materials only. The process is
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inadequate for the deposition of dielectric films because of charging, arcing, and very low deposition rates. Radio frequency (rf) sputtering is suitable for both conducting and nonconducting materials. A high frequency generator (13.56 MHz) is connected between the electrodes of the system. The oscillating rf potential applied between the anode and cathode modifies the electron motions, which produces better energy coupling to the electrons as well as higher plasma densities. A large capacitor (500-2000 pF), placed in series between the rf power supply and the powered electrode, allows a significant negative bias to develop on the cathode, typically half of the value of the applied peak-to-peak rf voltage. This bias is then the acceleration voltage for ions from the plasma, which move much too slowly to respond to the applied rf potentials. In addition to the series capacitor, usually, two other tuning components help in matching the impedance of the plasma to the output impedance of the rf power supply. These components, usually a shunt capacitor to ground and a series inductor, are located along with the series capacitor in the “matching network”. The inductor is fixed, and both of the capacitors (shunt and series) are variable. The reflected power is minimized by adjusting these variable capacitors in the tuning network. In rf sputtering, the substrates function as partial cathodes in the circuit and are bombarded by ions from the plasma, but at a lower rate than the primary cathode.

Magnetron sputtering uses a magnetic field to confine the electrons close to the cathode, making it easier to sustain an electrical discharge at low pressure. The conventional, circular planar cathode is characterized by high levels of erosion on the cathode surface in the form of a ring. This technique is particularly useful when high deposition rates and low substrate temperatures are required [15]. Both reactive and nonreactive forms of dc, rf and magnetron sputtering
have been employed for the deposition of compound semiconductors. In reactive sputtering, the reactive gas is introduced into the sputtering chamber along with argon to deposit thin films. For example, to deposit metal oxide thin films, a pure metal target is sputtered in a mixture of argon and oxygen atmosphere. The deposition rates and properties of the films strongly depend on the sputtering conditions such as the partial pressure of the reactive gas, the sputtering pressure, substrate temperature, and substrate to target spacing.

In sputter deposition, the material arrives at the substrate mostly in atomic or molecular form. The atom diffuses around the substrate with a motion determined by its binding energy to the substrate, which is influenced by the nature and temperature of the substrate. The depressions on the substrate surface act as adsorption sites for the diffusing atoms. At each hop, the atom will either jump over the barrier into an adjacent site or will re-evaporate. After a certain time, the atom will either evaporate from the surface or will join another diffusing single atom to form a doublet. These doublets will be joined by 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 will grow in size and it will lead to the coalescent stage. Coalescence proceeds until the film reaches continuity.

The process of rf sputter deposition is made possible due to the large difference in mass, and hence mobility, of electrons and inert gas ions. Being less massive than ions, electrons attain much greater velocities and travel much further than ions during each cycle of the applied rf voltage waveform. Hence they eventually accumulate on the target, substrate, and chamber walls such that the plasma is the most positive potential in the system. These induced negative
voltages or “sheath voltages” [16] cause acceleration of positive ions toward the negatively charged surfaces, which subsequently leads to sputtering events. The volume adjacent to the cathode surface relatively free of electrons leads to a “dark space” because electrons are not available to excite gas atoms. The target is selectively sputtered by controlling the relative surface areas of the target and the substrate holder. If space charge limited current is assumed, the ion current flux, $J$ can be estimated by the Child-Langmuir equation [17],

$$J = \frac{KV^{3/2}}{D^2 m_{\text{ion}}}$$  \hspace{1cm} (2.1)

where, $D$ is the dark space thickness, $V$ is the sheath voltage, $m_{\text{ion}}$ is the ionic mass and $K$ is the proportionality constant. Since the positive ion current must be equal at both the electrodes,

$$\frac{A_A V^{3/2}_A}{D_A^2} = \frac{A_B V^{3/2}_B}{D_B^2}$$  \hspace{1cm} (2.2)

where, $A_A$ and $A_B$ are the surface areas of cathode and anode $A$ and $B$ respectively. If positive ion current densities are assumed to be equal, there would be a much greater positive ion current flowing during one half cycle of the applied voltage waveform than the other due to the much greater area of the grounded substrate electrode. Here, as the system is assumed to be in steady state, the total positive ion current per half cycle should be the relevant quantity.

The glow discharge itself is a region where large quantities of positive and negative charges exist and can be modelled as a wire. Since most of the voltage in the glow discharge is dropped across the dark space, and they have very low conductivities, they can be modelled as capacitors such that the capacitance $C$,
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\[ C \propto A/D \quad \text{(2.3)} \]

Furthermore, an ac voltage will divide across the two series capacitors such that,

\[ \frac{V_A}{V_B} = \frac{C_B}{C_A} \quad \text{(2.4)} \]

\[ \therefore \frac{V_A}{V_B} = \left( \frac{A_B}{A_A} \right)^2 \quad \text{(2.5)} \]

This equation tells that smaller area will see larger sheath voltage, whereas larger area will see a smaller sheath voltage by a power of 2. The usefulness of this result is that \( A_B > A_A \) must hold to selectively sputter the target. This is done in practice by grounding the substrate holder to the entire chamber resulting in a very large \( A_B \). For this reason it is extremely important that the substrate holder and the system are well grounded to ensure that re-sputtering of the growing film does not occur.

Sputtering yield is defined as the quantity of the material sputtered per ion (atoms/ion or grams/ion) [18]. Main features observed for the sputtering technique are:

1) Sputtering yield differs with the nature of the element i.e., the yield increases as the reciprocal of the binding energy of the surface atoms.
2) Sputtering yield decreases as the surface damage increases i.e. the yield from a rougher surface is lower than that from a smoother surface.
3) As the mass of the sputtering species increases, the sputtering yield increases.
4) Lighter mass ions penetrate deeper into the target than heavier mass ions.
5) As sputtering energy increases, the sputtering yield increases up to an energy of 100 keV. At higher energies, the sputtering yield again decreases since the ions penetrate into the target. Since smaller particles penetrate further into the target, the energy when the yield starts to decrease is lower for lighter particles.

6) For multicomponent samples, the lightweight particle is usually preferentially sputtered if the binding energies of the components are similar. The sputtering rate of each component increases as the reciprocal of the binding energy and mass of that component.

7) Sputtering of oxide targets results in preferential depletion of oxygen.

8) Sputtering yield of metal oxide is less than that of corresponding metals.

9) For oxide samples, sputtering in an oxygen rich environment decreases the sputtering yield; the sputtering yield does not vary in other environments (for example, CO and N₂) indicating that adsorption without chemical bonding is not enough to reduce the sputtering yield.

In the present study, an in-house assembled magnetron has been used for rf magnetron sputtering. A magnet of 2000 gauss was used to deflect the ions. A schematic diagram of the magnetron is shown in figure 2.2. The vacuum system consists of a 6” diameter diffusion pump backed by a rotary pump (make - Indovision, Bangalore). The rf supply was connected to the magnetron through a capacitive matching network (Digilog Instruments, Bangalore). The flow of argon gas into the vacuum chamber was controlled using a mass flow controller (Bronkhorst, Holland).
2.3.3 Pulsed laser deposition (PLD)

Lasers are energy sources in the form of monochromatic and coherent photons, enjoying ever increasing popularity in diverse and broad applications. The laser has become an irreplaceable tool in metallurgy, medical technology and electronic industry. In material science, lasers play a significant role either as a passive component for process monitoring or as an active tool by coupling its radiation energy to the material being processed. Lasers, are therefore, extremely useful in a wide variety of applications such as localized melting during optical pulling, laser annealing of semiconductors, surface cleaning by desorption and ablation, laser induced rapid quench to improve surface hardening etc. Finally, pulsed laser deposition (PLD) has emerged as one of the premier thin film deposition technologies [19].

PLD is the deposition method of choice when one needs to deposit materials with complex stoichiometry. PLD was the first technique successfully used to deposit a superconducting YBa$_2$Cu$_3$O$_{7-d}$ thin film. Since then, many materials, especially multi element oxides, normally difficult to be deposited by other methods, have been deposited by PLD. This technique offers many potential applications, from integrated circuits and optoelectronics to micro mechanics and medical implants.

In a typical PLD process, a focused train of high energy laser pulses, derived from a UV nanosecond pulse width laser source, such as the frequency tripled (355 nm) or quadrupled (266 nm) solid state Nd:YAG laser, or the KrF (248 nm) or ArF (193 nm) excimer laser, is rastered over either a metal, a single crystal oxide or a compressed oxide powder target in a vacuum chamber. The high energy laser pulses interact with the target generating a plume comprised of
atomic and molecular species ablated from the target. A substrate, often heated, is placed at a short distance from the target in the direction of the advancing plume (figure 2.3). Though the actual physical process of material removal is quite complex, one can consider the ejection of material to occur from rapid explosion of the target surface by superheating. Unlike thermal evaporation, which produces a vapor composition dependent on the vapor pressures of elements in the target material, the laser induced expulsion produces a plume of material with stoichiometry similar to the target. The best quality films can be deposited by controlling the fundamental criteria such as the substrate temperature, the relative and absolute arrival rates of atoms and the energy of the depositing flux. PLD offers the best control over these criteria than other vacuum deposition techniques.

Figure 2.3. Schematic diagram of PLD chamber
The main advantages of pulsed laser deposition are:

1) **conceptually simple**: a laser beam vaporizes a target surface, producing a film with the same composition as the target.

2) **versatile**: many materials can be deposited in a wide variety of gases over a broad range of gas pressures.

3) **cost effective**: one laser can serve many vacuum systems.

4) **fast**: high quality samples can be grown reliably in 10 or 15 minutes.

5) **scalable**: as complex oxides move toward volume production.

The mechanism of pulsed laser deposition, in contrast to the simplicity of the setup, is a very complex physical phenomenon. It not only involves the physical process of the laser-material interaction, but also the formation of plasma plume with high energetic species and even the transfer of the ablated material through the plasma plume onto the substrate surface. Thus the thin film formation in PLD generally can be divided into the following four stages.

1) Laser radiation interaction with the target

2) Dynamics of the ablated materials.

3) Deposition of the ablation materials on the substrate.

4) Nucleation and growth of a thin film on the substrate surface

Each stage in PLD is critical to the formation of quality epitaxial, crystalline, stoichiometric and uniform thin films.

In the first stage, the laser beam is focused onto the surface of the target. At sufficiently high flux densities and short pulse duration, all elements in the target are rapidly heated up to their evaporation temperature. Materials are dissociated from the target surface and ablated out with stoichiometry as in the target. The instantaneous ablation rate is highly dependent on the fluences of the
laser shining on the target. The ablation mechanisms involve many complex physical phenomena such as collision, thermal and electronic excitation, exfoliation and hydrodynamics.

During the second stage, the emitted materials tend to move towards the substrate according to the laws of gas dynamics and show the forward peaking phenomenon. The spatial thickness varies as a function of $\cos \theta$. The spot size of the laser and the plasma temperature have significant effects on the deposited film uniformity. The target-to-substrate distance is another parameter that governs the angular spread of the ablated materials. A mask placed close to the substrate can reduce the spreading. Typical plasma temperature measured by emission spectroscopy during initial expansion of the plume is $\approx 10,000$ K, which is well above the boiling point of most materials ($\approx 3000$ K). Heating of the plasma to these temperatures is thought to occur by inverse Bremsstrahlung absorption of the laser light in a free transition of electron ion pair. This high temperature would evaporate the surface layer of the target thereby producing exact composition in the thin films.

The third stage is important to determine the quality of thin film. The ejected high energy species impinge onto the substrate surface and may induce various types of damage to the substrate. These energetic species sputter some of the surface atoms and a collision region is formed between the incident flow and the sputtered atoms. Film grows after a thermalized region is formed. The region serves as a source for condensation of particles. When the condensation rate is higher than the rate of particles supplied by the sputtering, thermal equilibrium condition can be reached quickly and films grow on the substrate surface at the
expense of the direct flow of the ablation particles and the thermal equilibrium obtained.

The effect of increasing the energy of the adatoms has a similar effect of increasing substrate temperature on film growth. Typical power densities involved in PLD are approximately 50 MWcm$^{-2}$ for a reasonable growth rate. (> 1 Å$^2$/shot) If plasma is formed during laser target interaction in vacuum or in air then an explicit laser-plasma interaction occurs due to which ions in the plasma are accelerated to as much as 100-1000 eV [20].

Nucleation and growth of crystalline films depend on many factors such as the density, energy, ionization degree, and the type of the condensing material, as well as the temperature and the physio-chemical properties of the substrate. The two main thermodynamic parameters for the growth mechanism are the substrate temperature $T$ and the supersaturation $D_m$ related by the following equation:

$$D_m = kT \ln(R/R_e)$$  (2.6)

where, $k$ is the Boltzmann constant, $R$ is the actual deposition rate, and $R_e$ is the equilibrium value at the temperature $T$.

The nucleation process depends on the interfacial energies between the three phases present - substrate, the condensing material and the vapour. The critical size of the nucleus depends on the driving force, i.e. the deposition rate and the substrate temperature. For the large nuclei, a characteristic of small supersaturation, they create isolated patches (islands) of the film on the substrate, which subsequently grow and coalesce together. As the supersaturation increases, the critical nucleus shrinks until its height reaches on atomic diameter and its shape is that of a two dimensional layer. For large supersaturation, the layer-by-layer nucleation will happen for incompletely wetted foreign substrates.
The crystalline film growth depends on the surface mobility of the adatom (vapour atoms). Normally, the adatom will diffuse through several atomic distances before sticking to a stable position within the newly formed film. The surface temperature of the substrate determines the adatom's surface diffusion ability. High temperature favours rapid and defect free crystal growth, whereas low temperature or large supersaturation crystal growth may be overwhelmed by energetic particle impingement, resulting in disordered or even amorphous structures.

The mean thickness, \( N \), at which the growing thin and discontinuous film reaches continuity, is given by the formula:

\[
N = A(1/R)^{1/3} \exp(-1/T)
\]

where \( A \) is a constant related to the materials and \( R \) is deposition rate. In the PLD process, due to the short laser pulse duration (\( \sim 10 \) ns) and hence the small temporal spread (\( \leq 10 \) ms) of the ablated materials, the deposition rate can be enormous (\( \sim 10 \) nm/s). Consequently a layer-by-layer nucleation is favoured and ultra-thin and smooth film can be produced. In addition, the 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.

In the present study, PLD was used to deposit the oxide films at room temperature. The process was carried out in a vacuum chamber pumped by a 6” diffusion pump backed by a rotary pump (Indovision, Bangalore). The source used was the third(355 nm) harmonic of Nd:YAG laser (Spectra Physics model GCR 150). The flow of oxygen into the chamber was controlled using a mass flow controller (Bronkhorst, Holland).
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2.4 Charactersation tools

Once the films are grown, the structural, compositional, morphological, optical and electrical analytical tools give a better understanding of the film behavior and characteristics. On the reverse, the characterisation techniques help in optimizing the growth conditions to get device quality films. In the following sections, the techniques used for the film characterisations in the present study are discussed briefly.

2.4.1 Thin film thickness

Film thickness has a crucial role in determining its properties unlike a bulk material. The properties of the thin films can be reproduced if thickness, along with other deposition parameters, is kept constant. Film thickness may be measured either by in situ monitoring of the rate of deposition or after the film deposition. The thickness of the thin films prepared for the work presented in this thesis was measured by a stylus profiler (Dektak 6M).

The stylus profiler takes measurements electromechanically by moving the sample beneath a diamond tipped stylus. The high precision stage moves the sample according to a user defined scan length, speed and stylus force. The stylus is mechanically coupled to the core of a linear variable differential transformer (LVDT). While in contact over the moving sample surface, surface variations cause the stylus to be translated vertically. Electrical signals corresponding to the stylus movement are produced as the core position of the LVDT changes. The LVDT scales an ac reference signal proportional to the position change, which in turn is conditioned and converted to a digital format through a high precision, integrating, analog-to-digital converter [21].
To measure the film thickness, a region of the substrate has to be masked during film deposition. This creates a step on the sample. The thickness of the sample can then be measured accurately by measuring the vertical motion of the stylus over the step.

2.4.2 Structural characterisation

The crystallographic nature of a sample very well influences its electrical and optical properties. X-ray diffraction (XRD) studies are generally used for structural analysis. Any material has a characteristic diffraction pattern, whether present in pure state or as one constituent of a mixture of substances. This fact is made useful in the diffraction method of chemical analysis. The advantage of the technique is that it discloses the presence of a substance, as that substance actually exists in the sample and not in terms of its constituent chemical elements. Hence, diffraction analysis is useful whenever it is necessary to know the state of chemical combination of the elements involved or the particular phase in which they are present. Compared with ordinary chemical analysis the diffraction method has the advantage that it is usually much faster, requires only very small quantity of sample and is non-destructive.

The basic law involved in the diffraction method of structural analysis is the Bragg’s law. When monochromatic beam of x-rays impinges upon the atoms in a crystal lattice, each atom acts as a scattering source. The crystal lattice presents a series of parallel reflecting planes to the incident x-ray beam. The intensity of the reflected beam at certain angles will be maximum when the path difference between two reflected waves from two different crystal planes is an integral multiple of $\lambda$. This condition is termed as Bragg’s law and is given by,

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

(2.8)
where, \( n \) is the order of diffraction, \( \lambda \) is the wavelength of x-rays, \( d \) is the spacing between consecutive parallel planes and \( \theta \) is the glancing angle (or the complement of the angle of incidence) [22].

X-ray diffraction studies give a whole range of information about the crystal structure, orientation, average crystalline size and stress in the powder. Experimentally obtained diffraction patterns of the sample are compared with the standard powder diffraction files published by the International Centre for Diffraction Data (ICDD).

In the present study, the bulk and thin film samples were structurally characterized by recording their XRD patterns using an automated Rigaku X-ray diffractometer. The filtered copper K\(_\alpha\) radiation (\( \lambda = 1.5414 \ \text{Å} \)) was used for recording the diffraction pattern. The average grain size, \( t \), of the film can be calculated using the Scherrer’s formula,

\[
t = \frac{0.9\lambda}{\beta \cos \theta}
\]  

Here, \( \beta \) is the full width at half maximum in radians.

The lattice parameter values for a cubic crystallographic system can be calculated from the following equation using the (hkl) parameters and the interplanar spacing \( d \).

\[
\text{Cubic system,} \quad \frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}
\]
2.4.3 Morphological analysis

Surface morphology is an important property while going for multilayer device fabrication. Roughness of the thin film surface plays a vital role, especially while making interfaces. Some of the characterisation tools used to study about the surface of thin films is described below.

i. Scanning Electron Microscope (SEM)

The scanning electron microscope (SEM) uses electrons rather than light to form an image. SEM has several advantages over an ordinary light microscope [23]. The SEM has a large depth of field, which allows a large amount of the sample to be in focus at a time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. Preparation of the samples is relatively easy since most SEMs only require that sample should be conductive. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation makes the SEM one of the most heavily used instruments in current research areas.

In a typical SEM, electrons are thermionically emitted from a tungsten or lanthanum hexaboride (LaB₆) cathode and are accelerated towards an anode. Alternatively, electrons can be emitted via field emission. The most common is the tungsten hairpin gun. Tungsten is used because it has the highest melting point and lowest vapour pressure of all metals, thereby allowing it to be heated for electron emission.

A voltage is applied to the loop, causing it to heat up. The anode, which is positive with respect to the filament, forms powerful attractive forces for electrons. This causes electrons to accelerate toward the anode. The anode is
arranged, as an orifice through which electrons would pass down to the column where the sample is held.

The electron beam, which typically has an energy ranging from a few hundred eV to 100 keV, is attracted through the anode, made to pass through a condenser lens, and focused to very fine point on the sample by the objective lens (figure 2.4). The electron beam hits the sample, producing secondary electrons from the sample. These electrons are collected by a secondary detector or a backscatter detector and converted to voltage, and amplified. The amplified voltage is applied to the grid of the CRT that causes the intensity of the spot of
light to change. The image consists of thousands of spots of varying intensity on the face of a CRT that corresponds to the topography of the sample.

The spatial resolution of the SEM depends on the size of the electron spot, which in turn depends on the electron energy and the magnetic electron-optical system which produces the scanning beam. To ensure that the information recorded in the image arises only from the sample surface, the column must always be at vacuum. Or else, there are chances for contamination of the sample and the electron beam, instead of being directed onto the sample, would induce ionisation in any background gas that would effect the measurement being made on the sample.

In the present studies, JEOL JSM 5600 was used for SEM analysis.

ii. Atomic Force Microscopy (AFM)

The atomic force microscope (AFM) is a very high resolution type of scanning probe microscope, with resolution of fractions of a nanometer, more than 1000 times better than the optical diffraction limit. It can, therefore, probe into understanding the fine details of a sample surface [23].

In atomic force microscopy, a tip integrated to the end of a spring cantilever, is brought within the inter atomic separations of a surface, such that the atoms of the tip and the surface are influenced by inter atomic potentials. As the tip is rastered across the surface, it bounces up and down with the contours of the surface. By measuring the displacement of the tip (i.e. the deflection of the cantilever), one can theoretically map out the surface topography with atomic resolution.
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The AFM is essentially identical in concept to the scanning profilometer, except that the deflection sensitivity and resolution are improved by several orders of magnitude. The AFM can operate well in ambient air or in a liquid environment making it an important tool in studying biological systems, polymers and a host of insulator and semiconductor materials.

![Diagram of AFM](image)

**Figure 2.5.** The essential elements of an AFM

An AFM images a surface in a manner analogous to the gramophone stylus sensing the grooves of gramophone disk. The essential elements of an AFM are shown in figure 2.5. The tip is attached to a cantilever type spring as shown in

![Diagram of tip and cantilever](image)

**Figure 2.6.** Attachment of the tip to the cantilever in an AFM
figure 2.6. As the tip and sample interact, forces act on the tip and cause the cantilever (spring) to deflect. The cantilever position is monitored by a position detector. The output of the detector is connected to a feedback controller that regulates the force between the sample and the tip by moving the sample up or down. The sample is moved by a PZT scanning actuator. The cantilever must be soft enough to deflect a measurable amount without damaging the surface features of the sample. The amount of deflection is proportional to the force acting on the tip:

\[ F_{\text{spring}} = -k \cdot \Delta Z \]  

(2.11)

where, \( F \) is the force on the sample, \( k \) is the spring constant of the cantilever, and, \( \Delta Z \) is the deflection of the cantilever.

Two important modes of an AFM are contact mode and the tapping mode. In the contact mode, the static tip deflection is used as the feedback signal. In the tapping mode, the cantilever is externally oscillated at or close to its resonance frequency. The oscillation amplitude, phase and resonance frequency are modified by tip-sample interaction forces; these changes in oscillation with respect to the external reference oscillation provide information about the sample's characteristics.

The AFM provides us with a true three dimensional surface profile compared to the two dimensional SEM image, with atomic resolution in ultra high vacuum environments. But an AFM can only image a maximum height of the order of micrometres and a maximum scanning area of around 150 by 150 micrometres whereas SEM can image an area of the order of millimetres by millimetres with a depth of field of the order of millimetres.
In the present work, AFM from Veeco was used for the morphological study.

2.4.4 Compositional analysis

Compositional analysis helps to check the stoichiometry of the deposited films. Some of the characterization tools used in the present investigation is described below.

i. Energy dispersive x-ray (EDX) analysis

Energy dispersive x-ray (EDX) analysis is used for determining the elemental composition of a specimen. It often works as an integrated feature of a SEM, and cannot operate on its own without the latter. During EDX analysis, the specimen is bombarded with an electron beam inside the scanning electron microscope. The bombarding electrons (primary electrons) collide with the specimen, knocking some of them off in the process. The vacancy in the specimen atoms created by the ejection of an inner shell electron is eventually occupied by a higher energy electron from an outer shell. During this transition, the transferring electron gives up its excess energy in the form of x-rays.

The amount of energy released by the transferring electron depends on which shell it is transferring from, as well as which shell it is transferring to. Furthermore, the atom of every element releases x-rays, unique in energy during the transferring process, characteristic of that element. Thus, by measuring the energy of the x-rays emitted by a specimen during electron beam bombardment, the identity of the atom from which the x-ray was emitted can be established.
The output of an EDX analysis is an EDX spectrum, which is a plot of how frequently an x-ray is received for each energy level. An EDX spectrum normally displays peaks corresponding to the energy levels for which the most x-rays had been received. Each of these peaks is unique to an atom, and therefore corresponds to a single element. The higher a peak in a spectrum, the more concentrated the element is in the specimen. An EDX plot not only identifies the element corresponding to each of its peaks, but the type of x-rays to which it corresponds as well. For example, a peak corresponding to the amount of energy possessed by x-rays emitted by an electron in the L-shell going down to the K-shell is identified as a $K_{\alpha}$ peak. The peak corresponding to x-rays emitted by M-shell electrons going to the K-shell is identified as a $K_{\beta}$ peak as shown in figure 2.7.
ii. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is an imaging technique whereby a beam of electrons is focused onto a specimen causing an enlarged version to appear on a fluorescent screen or layer of photographic film or to be detected by a CCD camera. The first practical transmission electron microscope was built by Albert Prebus and James Hillier at the University of Toronto in 1938 using concepts developed earlier by Max Knoll and Ernst Ruska. Electrons are generated by a process known as thermionic discharge in the same manner as the cathode in a cathode ray tube, or by field emission; they are then accelerated by an electric field and focused by electrical and magnetic fields onto the sample. The electrons can be focused onto the sample providing a resolution far better than possible with light microscopes, and with improved depth of vision. Details of a sample can be enhanced in light microscopy by the use of stains. Similarly with electron microscopy, compounds of heavy metals such as osmium, lead or uranium can be used to selectively deposit in the sample to enhance structural details. The electrons that remain in the beam can be detected using a photographic film, or fluorescent screen [24]. So areas where electrons are scattered appear dark on the screen, or on a positive image.

An additional class of these instruments is the electron cryomicroscope, which includes a specimen stage capable of maintaining the specimen at liquid nitrogen or liquid helium temperatures. This allows imaging specimens prepared in vitreous ice, the preferred preparation technique for imaging individual molecules or macromolecular assemblies. Another type of TEM is the scanning transmission electron microscope (STEM), where the beam can be rastered across the sample to form the image. In analytical TEMs the elemental
composition of the specimen can be determined by analysing its X-ray spectrum or the energy-loss spectrum of the transmitted electrons. Modern research TEMs may include aberration correctors, to reduce the amount of distortion in the image, allowing information on features on the scale of 0.1 nm to be obtained (resolutions down to 0.08 nm has been demonstrated, so far). Monochromators may also be used which reduce the energy spread of the incident electron beam to less than 0.15 eV.

From TEM images, size of the nanoparticles can be determined. Parallel lines in the high resolution transmission electron micrograph (HRTEM) represent planes in the crystal lattice and distance between them corresponds to d spacing. By comparing these d spacing values with the JCPDS data, one can identify the orientation of the planes in the synthesized material. Selective area electron diffraction (SAED) is the map of the reciprocal lattice which will also give the signature of various planes in which material has been grown. Depending on the crystalline nature of the material, the SAED pattern will be orderly arranged spots, distinguishable rings or fused rings. But in the case of quantum dots concentric rings are observed in the SAED. The d spacing of the planes corresponding to the rings can be determined by the following equation

\[ (Dd) = CL\lambda \]  

(2.12)

where \( L \) is the effective camera length, \( \lambda \) is the de-Broglie wavelength of the accelerating electrons, \( D \) is the ring diameter of a standard electron diffraction pattern and \( d \) is the interplanar spacing [24]. The term on the right hand side of the equation is referred to as the camera constant. TEM, JEOL operating at an accelerating voltage of 200 kV was used for the confirmation of the formation of nanorods in the present work.
2.4.5 Electrical transport properties

i. Hall effect measurement

The Hall effect measurement technique is widely applied in the characterisation of semiconductor materials as it gives the resistivity, the carrier density, type of carriers and the mobility of carriers. When a magnetic field is applied to a conductor perpendicular to the current flow direction, an electric field will be developed perpendicular to the direction of magnetic field and the current. This phenomenon is known as Hall effect and the developed voltage is called Hall voltage.

The force acting on a charge \(q\) moving with a velocity \(v\) in the presence of electric \((E)\) and magnetic \((B)\) fields is given by the vector expression

\[
\vec{F} = q(\vec{E} + \vec{v} \times \vec{B})
\]

(2.13)

For n-type and p-type samples, the electrons and holes respectively deflect to the same side of the sample for the same current direction because electrons flow in the opposite direction to holes and have opposite charge.

The Hall coefficient \(R_H\) is defined as

\[
R_H = \frac{V_H d}{B I}
\]

(2.14)

where \(d\) is the sample dimension in the direction of magnetic field \(B\), \(V_H\) is the Hall voltage and \(I\) is the current through the sample [23]. Hall coefficient is related to hole \((p)\) and electron \((n)\) densities by the equation:

\[
p = \frac{1}{qR_H}; \quad \text{and} \quad n = -\frac{1}{qR_H}
\]

(2.15)
Equation 2.15 is derived under the assumption of energy independent scattering mechanisms. With this assumption relaxed, the expressions for the hole and electron densities become

\[ p = \frac{r}{qR_h}; \quad \text{and} \quad n = -\frac{r}{qR_h} \quad (2.16) \]

where \( r \) is the Hall scattering factor, defined by \( r = \langle \tau^2 \rangle / \langle \tau \rangle \), with \( \tau \) being the mean time between carrier collisions. The scattering factor depends on the type of scattering mechanism in the semiconductor and generally lies between 1 and 2. For lattice scattering, \( r = 1.18 \), for impurity scattering \( r = 1.93 \), and for neutral impurity scattering \( r = 1 \). The scattering factor is also a function of magnetic field and temperature and can be determined by measuring \( R_h \) in the high magnetic field limit, i.e.,

\[ r = \frac{R_h(B)}{R_h(B = \infty)} \quad (2.17) \]

In the high field limit \( r \to 1 \).

Figure 2.8: Lamella-type van der Pauw Hall sample.
The Hall mobility $H$ is defined by

$$H = \frac{|R_H|}{\rho} = \frac{|R_H|}{\sigma}$$

(2.18)

substituting the value of $\sigma$ for hole and electron, the equation 1.6 becomes

$$\mu_H = \tau_H \mu_e; \quad \text{and} \quad \mu_H = r \mu_e$$

(2.19)

for extrinsic p- and n-type semiconductors, respectively. Hall mobilities can differ significantly from conductivity mobilities since $r$ is generally larger than unity. For most Hall-determined mobilities, $r$ is taken as unity.

A more general geometry is the irregularly shaped sample in figure 2.8. The theoretical foundation of Hall measurement evaluation for irregularly shaped samples is based on conformal mapping developed by van der Pauw. He showed how the resistivity, carrier density, and mobility of a flat sample of arbitrary shape can be determined without knowing the current pattern if the following conditions are met: contacts should be point contacts located symmetrically on the periphery of the sample, the sample is uniformly thick, and does not contain isolated holes. This is not achievable in practice, and some error is introduced thereby. Hall effect measurements are simple to interpret for uniformly doped samples. However in delafossite compounds it was very difficult to determine the hall coefficient owing to the low mobility values. The efforts to measure the carrier concentration in p-type delafossites did not succeed due to the observation of unpredictable dependence of Hall voltage on magnitude and direction of applied magnetic field. The hall voltage showed a non linear behaviour as function of applied magnetic field and did not change sign with reversing the direction of the applied magnetic field. Such an electrical behaviour has been attributed to mixed conduction. Hence in the case of p-type conductors, the type
of carriers was determined by the thermopower measurement which showed positive Seebeck coefficient. The hall coefficient of n-type carriers was determined as described using van der Paw geometry.

The pn junctions were investigated by fabricating the heterojunctions and studying their current voltage characteristics using the Keithley source measure unit SMU236.

ii. Thermopower measurements

The sample holder for the thermopower measurement is similar to the one reported by Young et. al. [25]. The sample holder is made from copper and can be thermally attached to a closed cycle two stage cryostat. The copper blocks ‘F’ and ‘G’ are electrically isolated from each other and also from the sample-holder stage, but thermally connected via a sheet of 2 mm thick teflon. The heating element in the blocks is carbon resistance (100Ω) mounted with stycast™ epoxy in hole bored through the centre of the heating blocks parallel to its axis. Embedded in, but electrically isolated from, the heater block is a type ‘K’ differential thermocouple made from chromel alumel. The junctions of the chromel alumel differential thermocouple are located as close as possible (Below 1mm from the surface of the blocks F,G where the samples are mounted) to the mounting surface of the heater block and are thermally anchored which stycast™ epoxy.

All the thermocouple junctions are located just under the surface of the copper blocks exactly where the sample is loaded. Both of them are drilled and tapped with holes on the inside of the channel between the blocks. All of the wires exiting the sample holder are wound in twisted pairs to minimise magnetic
interference and these pairs are wound around the cryostat expander arm multiple times to minimise heat conduction [26].

The two ends of the thermocouple and the ends of the heater resistor are connected to the PID – temperature controller which controls the temperature gradient between the blocks.

The objective of the temperature controller is to maintain a temperature difference of 1°C between the two copper blocks of the experimental set-up in order to facilitate the thermo e.m.f. measurement of the thin film sample A differential thermocouple. (type K, cromel-alumel) is used owing to the convenience it offers in the measurement of temperature difference and also due to its low thermal inertia which supports good control. However, the sensitivity of a thermocouple is relatively low, only about 40μV/°C in the case of a type-K thermocouple. This is a serious challenge, as it demands a high performance amplifier capable of amplifying microvolt level signal with the required accuracy. It is not easy to construct such an amplifier using locally available components hence an existing micro voltmeter (Model – KEITHLY 2000) is used for temperature measurement. A personnel computer is used to implement the control function, which communicates with the micro voltmeter through IEEE-488 interface. The heater voltage is calculated using PID control algorithm and it is sent to the heater through a D/A channel of an analogue interface which is inserted into one of a bus expansion slot of the PC. The entire control programme that also includes provision for a real-time graphical display of the control parameter is written in C-language.
2.4.6 Optical studies

i. Diffuse reflectance spectroscopy (DRS)

In the present study, diffuse reflectance spectroscopy and transmission spectroscopy were used to determine the band gap of powder and thin film samples respectively.

Diffuse reflection is the reflection of light from an uneven or granular surface such that an incident ray is seemingly reflected at a number of angles. Diffuse reflected rays from a sample do not obey the Snell’s law as do the ordinary mirror-like specular reflections. The measurement of radiation diffusely reflected from a surface constitutes the area of spectroscopy known as diffuse reflectance spectroscopy (DRS). Specular reflection is due to the reflection at the surface of single crystallites while diffuse reflection arises from the radiation penetrating into the interior of the solid and re-emerging to the surface after being scattered numerous times. Thus, the DRS spectra can exhibit both absorbance and reflectance features due to contributions from transmission, internal and specular reflectance components as well as scattering phenomena in the collected radiation.

Based on the optical properties of the sample, several models have been proposed to describe the diffuse reflectance phenomena. The Kubelka-Munk (KM) model put forward in 1931 [27, 28] is widely used and accepted in DRS. The KM theory is based on a continuum model where reflectance properties are described by differential equations for infinitesimally small layers. When the depth of the sample is infinite, the theory is solved to arrive at the remission function or the so-called KM function,
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\[
f(r_x) = \frac{(1 - r_x)^2}{2r_x} = \frac{k}{s} \quad (2.20)
\]

where, \( r_x = R_x(\text{sample})/R_x(\text{standard}) \), \( R_x \) denotes the diffuse reflectance. Here the standard used is BaSO\textsubscript{4}. \( R_x(\text{standard}) \) is taken as unity. The intensity of the diffusely reflected light therefore depends on the scattering coefficient \( s \) and the absorption coefficient \( k \). The band gap is estimated from the plot of \( \{(k/s)h\nu\}^2 \) versus \( h\nu \) (\( h\nu \) is the photon energy) by extrapolating the graph to the \( x \) axis.

DRS was carried out using Jasco V 500 spectrophotometer in the present studies.

ii. Transmission spectroscopy

Intrinsic optical absorption of a single photon across the band gap is the dominant optical absorption process in a semiconductor. When the energy of the incident photon (\( h\nu \)) is larger than the band gap energy the excitation of electrons from the valence band to the empty states of the conduction band occurs. The light passing through the material is then absorbed and the number of electron hole pairs generated depends on the number of incident photons \( S_0(\nu) \) (per unit area, unit time and unit energy). The photon flux \( S(x,\nu) \) decreases exponentially inside the crystal according to the relation,

\[
S(x, \nu) = S_0(\nu) \exp(-\alpha x) \quad (2.21)
\]

where, the absorption coefficient \( \alpha \), \( \alpha(\nu) = 4\pi k\nu/c \) is determined by the absorption process in semiconductors and \( k \) is the extinction coefficient.

For the parabolic band structure, the relation between the absorption coefficient \( \alpha \) and the band gap of the material is given by [29],
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\[ \alpha = \frac{A}{h\nu} (h\nu - E_g)^r \]  \hspace{1cm} (2.22)

where, \( r = 1/2 \) for allowed direct transitions, \( r = 2 \) for allowed indirect transitions, \( r = 3 \) for forbidden indirect transitions and \( r = 3/2 \) for forbidden direct transitions. \( A \) is the parameter which depends on the transition probability. The absorption coefficient can be deduced from the absorption or transmission spectra using the relation,

\[ I = I_0 e^{-\alpha t} \]  \hspace{1cm} (2.23)

where, \( I \) is the transmitted intensity and \( I_0 \) is the incident intensity of light and \( t \) is the thickness of the film. In the case of direct transition, \( (\alpha h\nu)^2 \) will show a linear dependence on the photon energy \( (h\nu) \). A plot of \( (\alpha h\nu)^2 \) against \( h\nu \) will be a straight line and the intercept on energy axis at \( (\alpha h\nu)^2 \) equal to zero will give the band gap energy. The transmission of the thin films was recorded using Jasco V570 spectrophotometer in the present studies. Further details of the experimental techniques are described in the respective chapters.
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References
