CHAPTER–II

2. Experimental details

2.1. Introduction

Synthesis of TCO materials with desired structure and properties is of prime importance in condensed matter physics and material science. Since the discovery of TCOs, there has been renewed interest in developing novel methods for the preparation of TCO thin films. The field of material science and engineering community’s ability to conceive the novel materials with an extraordinary combination of physical, chemical and mechanical properties has changed the modern society. There is an increasing technological progress. Modern technology requires thin films for distinct applications [1].

Thin film technology is the basic of astounding development in the solid state electronics. The usefulness of the optical properties of metal films, and scientific curiosity about the behavior of two-dimensional solids has been responsible for the immense interest in the study science and technology of the thin films. Thin film studies have directly or indirectly advanced many new areas of research in solid state physics and chemistry which are based on phenomena uniquely characteristic of the thickness, geometry, and structure of the film [1]. This chapter deals with the description of the synthesis of the thin films and the equipment utilized for the growth of CdZnO thin films at different process conditions (substrate temperature, post sputter annealing temperature, oxygen flow rate and Cd sputter power) as well as the technique used for their structural, morphological, optical and electrical characterization. In addition, we present the details of the equipment used for the swift heavy ion irradiation (100 MeV O\textsuperscript{7+} and Au\textsuperscript{7+}) of the films.
2.2. **Methods used for thin film production:**

There are currently number of different processes available for the production of material formation [2-5]. The concern here is with thin film deposition techniques for forming layers in the thickness range of a few nanometers to about ten microns. Generally, thin film deposition technologies are classified in to two types: (A) physical processes & (B) chemical processes. The classification scheme is presented in fig. 2.1.

![Classification scheme of thin film process](image)

**A. Physical process or Physical vapour deposition:**

Physical process covers the deposition techniques which depend on the evaporation or ejection of the material from a source. i.e. evaporation or sputtering. PVD processes are environmentally friendly vacuum deposition techniques [6] consisting of three fundamental steps:

- The solid material to be deposited is physically converted to vapour phase by high temperature vacuum or gaseous plasma,
- The material in vapour phase is transported to the substrate surface in vacuum or partial vacuum (4-6 Pa)
- The vapour condenses on the substrate to form the desired thin films.
Variety of physical vapour deposition techniques such as thermal evaporation [7], e-beam evaporation [8], molecular beam epitaxy [9], pulsed laser deposition [10], ion plating [11], laser evaporation [12], dc/rf sputtering [13], glow discharge sputtering and dc/rf magnetron sputtering [14] have been employed for the growth the thin films. Each technique has specific advantages and disadvantages with respect to deposition parameters

2.2.1. Thermal evaporation:

One of the common methods of PVD is Thermal evaporation. This is a form of thin film deposition, which is a vacuum technology for applying coatings of pure materials to the surface of various objects. Thermal Evaporation [15-17] involves heating a solid material inside a high vacuum chamber, taking it to a temperature which produces some vapor pressure. Inside the vacuum chamber, even a relatively low vapor pressure is sufficient to raise a vapor cloud inside the chamber. This evaporated material now constitutes a vapor stream, which traverses the chamber and hits the substrate, sticking to it as a coating or film. Since, in most of the cases, the material is heated to its melting point and is liquid, it is usually located in the bottom of the chamber, often in some sort of upright crucible. The vapor then rises above this bottom source, and the substrates are held inverted in appropriate fixtures at the top of the chamber.

2.2.2. Electron beam evaporation:

Electron beam evaporation [18] is a PVD technique whereby an intense, electron beam is generated from a filament and steered via electric and magnetic fields to strike source material (e.g. pellets of Au) and vaporize it within the vacuum environment. At some point as the source material is heated via this energy transfer its surface atoms will have sufficient energy to leave the surface. At this point they
will traverse the vacuum chamber, at thermal energy (less than 1 eV), and can be used to coat a substrate positioned above the evaporating material. Average working distances are 300 mm to 1 meter. Since thermal energy is so low, the pressure in the chamber must be below the point where the mean free path is longer than the distance between the electron beam source and the substrate. The mean free path is the average distance an atom or molecule can travel in a vacuum chamber before it collides with another particle thereby disturbing its direction to some degree. This is typically around $3.0 \times 10^{-4}$ torr or lower.

2.2.3. Molecular beam epitaxy:

MBE [19-24] is a sophisticated, finely controllable method for growing single-crystal epitaxial films in a high vacuum ($10^{-11}$ torr). The films are formed on single-crystal substrates by slowly evaporating the elemental or molecular constituents of the film from separate Knudsen effusion source cells (deep crucibles in furnaces with cooled shrouds) onto substrates held at a temperature appropriate for chemical reaction, epitaxy, and re-evaporation of excess reactants. The furnaces produce atomic or molecular beams of relatively small diameter, which are directed at the heated substrate, usually silicon or gallium arsenide. Fast shutters are interposed between the sources and the substrates. By controlling these shutters, one can grow superlattices with precisely controlled uniformity, lattice match, composition, dopant concentrations, thicknesses, and interfaces down to the level of atomic layers. An additional important advantage of MBE is the low temperature requirement for epitaxy, which for silicon is in the range of 400 °C to 800 °C [23] and for gallium arsenide, 500 °C to 600 °C. The extremely limited product throughput, the complex operation, and the expensive equipment are, at present, the
major limitations of this promising deposition technology for production applications

2.2.4. **Pulse laser ablation or deposition:**

Pulsed laser deposition (PLD) is a growth technique in which the photon energy of a laser characterized by pulse duration and laser frequency interacts with a bulk material [25–27]. As a result, material is removed from the bulk depending on the absorption properties of the target materials. A laser pulse is focused onto the surface of the target (solid or liquid) in a vacuum chamber and thereby removes material. A significant removal of materials occurs above a certain threshold power density, and the ejected, partially ionized material forms a luminous ablation plume. The threshold power density required to create such plasma depends on the absorption properties of the target material, the laser wavelength, and pulse duration. Typical for excimer laser is a pulse length of 10 ns, for femtosecond excimer lasers it is in the range of 500 fs.

2.2.5. **Ion plating:**

Ion plating [28] is a deposition process that utilizes concurrent or periodic bombardment of the substrate and depositing atoms of film material by atomic-sized energetic particles. The bombardment prior to deposition sputter cleans the surface. Bombardment during deposition is used to obtain good adhesion, densify the depositing material, aid in chemical reactions, modify residual film/coating stress, and otherwise modify the structure, morphology, and properties of the depositing film or coating. It is important, for best results, that the bombardment be continuous between the cleaning and the deposition portions of the process in order to maintain an atomically clean interface.
2.2.6. Ionized cluster beam deposition:

Ionized cluster beam deposition (ICBD) or cluster beam deposition [29-33] is one of the most recent emerging technologies for the deposition of thin films with growth-control capabilities not attainable by other processes. ICBD deposition is one of several techniques classified as ion-assisted thin-film formation. The material to be deposited emerges and expands into a vacuum environment from a small nozzle of a heated confinement crucible, usually constructed of high-purity graphite. The vapor pressure within the crucible is several orders of magnitude higher than the pressure of the vacuum chamber so that the expanding vapor supercools. Homogeneous nucleation results in the generation of atomic aggregates or clusters of up to a few thousand atoms held together by weak inter-atomic forces. The clusters passing through the vacuum towards the substrate can, in part, be positively charged by impact ionization with an electron beam irradiation. Closely controlled accelerating voltages add energy to the ionized clusters which then impinge on the substrate, diffuse or migrate along the plane of the surface, and finally form a thin film with exceptional purity. The complete and detailed process is extremely complex but offers unprecedented possibilities of film formation once the fundamentals and engineering technology are fully understood and exploited.

2.2.7. Sputtering:

Sputtering was discovered in 1852 by Grove [34] while investigating discharge tubes using a silver needle cathode. Sputtering is the thin film deposition manufacturing process at the core of today’s semiconductors, disk drives, CDs, and optical devices industries. In an atomic level, the ejection of atomic or molecular species from the surface of the target due to bombardment of high energetic projectile ions is called sputtering. The sputtering process begins when a substrate
to be coated is placed in a vacuum chamber containing an inert gas (usually Argon) and a negative charge is applied to a target source material that will be deposited onto the substrate causing the plasma to glow. Sputtering takes place only when the kinetic energy of the bombarding particles is extremely high, much higher than normal thermal energies in the “Fourth state of nature” plasma environment. This can allow a much more pure and precise thin film deposition on the atomic level than can be achieved by melting a source material with conventional thermal energies.

### i. Principle:

The principle of sputtering is explained with the help of fig. 2.2. The energetic ions when incident on the target surface lead to different phenomenon \[35\]. The ion may strike the target and get reflected back in the form of a neutral atom or an ion. This phenomenon also leads to generation of secondary electrons, which are ejected out by an electron, ion, photon or neutral. Secondary electrons generally have energy less than those of incident particles helping to maintain the glow discharge or plasma. The incident ion can lead to structural rearrangement of the target material, generation of vacancies, interstitials and changes in electrical charge levels. The incident ion can be buried in the target material. This phenomenon is called ion implantation which is applied for doping of the silicon wafers to manufacture integrated devices. Lastly, it can lead to sputtering; where this ion ejects the atoms of the target material, which can get deposited on the substrate. Sputtering atoms coming to the substrate have energy of few keV (higher than evaporation). The substrate is bombarded by energetic electrons, neutral particles and photons. This may lead to damage of the substrate surface.
ii. **Sputter yield:**

Sputtering occurs whenever any particle strikes a surface with enough energy to dislodge an atom from the surface. The sputter yield is just the ratio of the number of emitted particles per incident particle:

\[
Y = \frac{\text{No. of emitted particles}}{\text{No. of incident particles}}
\]

The Sputtering yield is the most important parameter for characterizing the sputter process. Sputtering yields depend on several factors relating to the incident ion and target material \([36, 37]\). These factors include ion mass, ion energy, ion angle of incidence, atomic mass of the target atoms, target atomic structure, target surface binding energy and target texture. For virtually all practical cases, sputtering almost always utilizes ion bombardment, either with inert gas ions such as \(\text{Ar}^+\) and \(\text{Kr}^+\), or small molecular ions such as \(\text{N}_2^+\), \(\text{O}_2^+\), and so on. The yield for bombardment of a surface with an ion or an atom of the same energy will be virtually identical; physical sputtering relies on the transfer of physical momentum and kinetic energy from the incident particle to the surface atoms, and this is independent of the particle's charge.

At incident ion energies of a few eV or so up to 30–50 eV, there is very little sputtering. Early work (1960’s) \([38]\) suggested the presence of a sputter
threshold in this energy regime below which no sputtering occurred. This has been found to be slightly misleading, and it is now generally thought that the minimum ion energy for sputtering is the binding energy of the most-weakly-bound surface atom. The yields in this energy range are typically below $10^{-2}$ at 30–40 eV ion energies, and fall rapidly at lower ion energies to the $10^{-6}$ level and below.

At incident energies of 40 to 1000 eV, the incoming particle has more than sufficient energy to dislodge tens to hundreds of atoms. Knock-on sputtering characterizes the practical energy range used for most sputtering applications. There are several general characteristics of knock-on sputtering:

1. The sputter yield increases linearly (roughly) with incident ion energy.
2. The highest yield occur for the best mass match between the incident species and the solid.
3. Increasing the angle of incidence from normal incidence (straight down) to perhaps 50 degrees from normal can increase the yield significantly (1.5–3) for most materials.
4. An increase in the flux (ion current) results in a linear increase in the number of sputtered atoms.

Considering the above sputtering mechanism, Yamamura et al. [39] revised their old semi-empirical formulae [40, 41] by interpolating them to propose a new one (hereafter called *Yamamura formula*) for the energy dependence of sputtering yield $Y(E)$ of monoatomic solids for normal incidence of projectiles, as given by
where $E$ is projectile energy and $M_1, M_2$ are the masses of a projectile and a target atom in a.m.u., respectively, $U_s$ is the surface binding energy of a target material and $E_{th}$ is the sputter threshold energy.

### iii. Types of sputtering:

Sputter deposition has been around for nearly 150 years from the earliest days of gas discharges and plasma physics. Sputtering, whether with a simple diode or a magnetron diode, requires a working gas pressure in the mTorr to 1 Torr range. Most magnetrons are best operated at a few mTorr. Currently, sputter deposition is being practiced by number of high vacuum technologies. The most commonly used is magnetron sputtering, which is diode plasma. Another common technology is RF sputtering, which is used primarily for dielectrics. A third variant is to use an ion beam and remove the sample or target from direct contact with plasma. Hence, sputter deposition started with simple DC diodes, and it is best to use with more complicated variations.

In addition, due to the reactive nature of many freshly sputtered atom species, the residual or working gas needs to be fairly clean and often inert, such as Ar or Kr. Sputtering systems typically have a base pressure that is several orders of magnitude (at least two) below the operating pressure, and clean gas is introduced at the base pressure to bring the pressure up to the working level.

#### a. dc/rf sputtering:

In sputtering there are two means of operation: dc (diode and triode) and ac (radiofrequency), which also function in two configurations: magnetron dc (balanced and unbalanced) and magnetron ac (balanced and unbalanced).
The simplest source of ions for sputtering is provided by the well-known phenomenon of glow discharge due to an applied electric field between two electrodes in a gas at low pressure. The gas breaks down to conduct electricity when a certain minimum voltage is reached. Such an ionized gas is called plasma. Ions of the plasma are accelerated at the target by high electric field. When the ions impinge the target, atoms (or molecules) are ejected from the surface of the target into the plasma, where they are carried away and then get deposited on the substrate. This type of sputtering is called “dc sputtering” (figure 2.3).

In dc (diode) discharge, the cathode electrode is the sputtering target and the substrate is placed on the anode, which is often at ground potential. The applied potential appears across a region very near the cathode, and the plasma generation region is near the cathode surface. The cathode in dc discharge must be an electrical conductor, since an insulating surface will develop a surface charge that will prevent ion bombardment of the surface. This condition implies that dc sputtering must be used to sputter simple electrically conductive materials such as metals, although the process is rather
slow and expensive compared to vacuum deposition. An advantage of dc sputtering is that the plasma can be established uniformly over a large area, so that a solid large-area vaporization source can be established.

When the plasma ions strike the target, their electrical charge gets neutralized and they return to the process as atoms. If the target is an insulator, the neutralization process results in a positive charge on the target surface. This charge may reach a level where bombarding ions are repelled and the sputtering process stops. To continue the process, the polarity must be reversed to attract enough electrons from the plasma to eliminate surface charge. This periodic reversal of polarity is done automatically by applying a radio-frequency (rf) voltage on the target assembly. Thus, this type of sputtering is known as “RF sputtering”, (figure 2.4).

**Fig. 2.4** Basic elements of rf sputtering system

### b. Magnetron sputtering:

The term “magnetron” was originally used to describe tubes used to generate microwave power for RADAR applications. In dc/rf sputtering the electrons that are ejected from the cathode are accelerated away from the cathode and are not efficiently used for sustaining the discharge. In order to
increase the efficiency of the sputtering process, it is common for the sputtering source to have some magnetic confinement through a magnetron source. The purpose of the magnetic field is to spiral the electrons so that they have more chance of undergoing an ionizing collision thus enabling the plasma to be operated at a higher density. This type of sputtering is called “magnetron sputtering” and it can be used with both dc and rf sputtering.

A magnetron uses a static magnetic field configured at the cathode location. The magnetic field is located parallel to the cathode surface. Secondary electrons which are emitted from the cathode due to ion bombardment are constrained by this magnetic field to move in a direction perpendicular to both the electric field (normal to the surface) and the magnetic field. This is known as an $E \times B$ (E cross B) drift, which is also the basis for the Hall Effect. This drift makes electrons to move parallel to the cathode surface in a direction of 90 degrees away from the magnetic field. If the magnetic field is set up correctly, this $E \times B$ drift can be arranged to close on itself, forming a current loop of drifting secondary electrons (Fig. 2.5).

![Fig. 2.5 The magnetic field configuration for circular planar magnetron cathode](image)

This high current of electrons creates high-density plasma, from which ions can be extracted to sputter the target material, producing a magnetron sputter configuration [42]. The disadvantage of the magnetron sputtering
configuration is that the plasma is confined nearer to the cathode and is not available to active reactive gases in the plasma near the substrate for reactive sputter deposition. This difficulty can be overcome using an unbalanced magnetron configuration (see Fig. 2.6), where the magnetic field is such that some electrons can escape from the cathode region [43]. A disadvantage of the unbalanced magnetron is that the current of escaping electrons is not uniform, and also the plasma generated is not uniform.

c. **Reactive sputtering:**

Reactive sputtering is commonly used for the deposition of oxide and nitride thin films. There are two approaches to reactive deposition, one where the cathode is a metal plate, and the other where the cathode is composed of the material of interest to be deposited, for example, a nitride or an oxide. The latter case is usually complicated due to the nonconductive nature of many oxide and some nitride targets, require the use of rf power to the cathode, as well as the poor physical stability of many of these compounds. This last issue may result in cracking or shattering the compound target, or else in difficulties in bonding it to the cathode, which is usually water cooled.

A reactive sputtering system is shown in Fig. 2.7. In this system, the cathode is placed in a chamber with walls and a pumping system. The walls are important, because films will also be deposited and reacted there as well as on the sample and the cathode. Typically, a system like this would be operated with some partial pressure of an inert gas, such as Ar, and a partial pressure of a reactive species, such as O\textsubscript{2} or N\textsubscript{2}. The operation of this system can be described by observing the changes in the discharge kinetics as well as the-
Fig. 2.6 Schematic configuration of a- balanced magnetron (Intermediate) and b- unbalanced magnetron (Type-1 and Type-2) [43]

- vacuum system as a function of the partial pressure or flow of the reactive species. In Fig. 2.8, the deposition rate and the discharge voltage are plotted as a function of reactive gas flow rate. There is a constant inert gas pressure in this example, perhaps a few mTorr of Ar. At the far left side of these charts, where there is no reactive gas flow, the cathode is being sputtered with pure Ar and the deposited films are purely metallic. Films are deposited on the sample as well as the chamber walls. As the reactive gas flow is increased very little happens initially. The
reactive gas, oxygen for example, is being absorbed by the deposited films on the sample and the walls.

**Fig. 2.8** The deposition rate (Top) and discharge voltage (Bottom) as a function of reactive gas flow for the experiment shown in fig.2.7.

**B. Chemical process or Chemical vapour deposition:**

Chemical process or CVD [44] is a materials synthesis process whereby constituents of the vapor phase react chemically near or on a substrate surface to form a solid product. The deposition technology has become one of the most important means for creating thin films and coatings of a very large variety of materials essential to advanced technology, particularly solid-state electronics where some of the most sophisticated purity and composition requirements must be met. The main feature of CVD is its versatility for synthesizing both simple and complex compounds with relative ease at generally low temperatures. Both chemical composition and physical structure can be tailored by control of the reaction chemistry and deposition conditions.

**2.2.8. Sol-gel process:**

The sol-gel process [45] is a versatile solution process for making advanced materials, including ceramics and organic-inorganic hybrids. In general, the sol-gel process involves the transition of a solution system from a liquid "sol" (mostly
colloidal) into a solid "gel" phase. Utilizing the sol-gel process, it is possible to fabricate advanced materials in a wide variety of forms: ultrafine or spherical shaped powders, thin film coatings, fibers, porous or dense materials, and extremely porous aerogel materials.

2.2.9. **Spray pyrolysis:**

Spray pyrolysis [46] has been applied to deposit a wide variety of thin films. These films were used in various devices such as solar cells, sensors, and solid oxide fuel cells. It is observed that often the properties of deposited thin films depend on the preparation conditions. An extensive review of the effects of spray parameters on film quality is given to demonstrate the importance of the process of optimization. The substrate surface temperature is the most critical parameter as it influences film roughness, cracking, crystallinity, etc.

2.2.10. **Spin coating:**

Spin coating [47] has been used for several decades for the application of thin films. A typical process involves depositing a small puddle of a fluid resin onto the center of a substrate and then spinning the substrate at high speed (typically around 30000 rpm). Centripetal acceleration will cause the resin to spread to, and eventually off, the edge of the substrate leaving a thin film of resin on the surface. Final film thickness and other properties will depend on the nature of the resin (viscosity, drying rate, percent solids, surface tension, etc.) and the parameters chosen for the spin process. Factors such as rotational speed, acceleration and fume exhaust contribute to how the properties of coated films are defined. One of the most important factors in spin coating is repeatability. Subtle variations in the parameters that define the spin process can result in drastic variations in the coated film.
2.2.11. Plasma enhanced CVD (PECVD):

PECVD [48] is an excellent alternative for depositing a variety of thin films at lower temperatures than those utilized in CVD reactors without settling for a lesser film quality. For example, high quality silicon dioxide films can be deposited at 300 to 350 degrees centigrade while CVD requires temperatures in the range of 650 to 850 degrees centigrade to produce similar quality films. PECVD uses electrical energy to generate a glow discharge (plasma) in which the energy is transferred into a gas mixture. This transforms the gas mixture into reactive radicals, ions, neutral atoms and molecules, and other highly excited species. These atomic and molecular fragments interact with a substrate and, depending on the nature of these interactions, either etching or deposition processes occur at the substrate. Hence, film formation can occur on substrates at a lower temperature than is possible in the conventional CVD process, which is a major advantage of PECVD.

2.2.12. Metal-organic chemical vapour deposition:

Vapor-phase epitaxy (VPE) and MOCVD [49] are used for growing epitaxial films of compound semiconductors in the fabrication of optoelectronic devices. Composite layers of accurately controlled thickness and dopant profile are required to produce structures of optimal design for device fabrication.

2.3. Substrate cleaning:

During the production of various devices by using sophisticated thin film technique; the proper substrate cleaning is required for homogeneous and uniform thin film deposition with higher adherence.

The first step of substrate cleaning is to pre-clean the substrate in an ultrasonic cleaner filled with distilled water for 5-10 minutes. Then slides are dipped in the dilute chromic acid for 10 min. The substrates were wiped by clean cotton. During
this whole cleaning process the handling of slides should be done with care. For handling the substrate, metal tweezers were used. Then, it was cleaned again in the ultrasonic bath. After this the slides were rinsed with glass-wares cleaning detergent. It is important to use very dilute solution of cleaner, because it is difficult to remove it later. Again these slides were wiped by cotton. Finally these slides were rinsed by hot distilled water in ultrasonic cleaner for 40°C. The purpose of this was to remove all the traces of the detergent. The substrates have been air dried in clean area, because cleaned substrates can pick up the dust from air by electrostatic attraction at a remarkable rate. These slides were ready for to use as substrates for the thin film depositions [50].

2.4. Description of the reactive dc magnetron sputtering system:

V.R. Technologies, Bangalore, India make reactive dc magnetron sputtering system equipped with several imported accessories. Such a system installed in our laboratory and is employed for the present work. The photograph of the sputtering system is shown in below fig. 2.9. This is a box type water cooled chamber made up of stainless steel with front hinged door. The door is provided with a toughened glass view port for viewing the process during sputtering. The base plate is provided with necessary feedthroughs. The top plate of chamber is proved with port for fixing the target holders and shutters. The targets with dimensions of 2 inch diameter and 3-5 mm thickness of Zn (99.999% purity) and Cd (99.99% purity) were used in the present study. The vacuum chamber is pumped down using a diffusion pump (350 lit/min), which is backed up by a direct drive rotary pump (250 lit/min). A liquid nitrogen trap incorporated between the chamber and the diffusion pump minimized the oil vapor contamination of the chamber.
Vacuum measurement is made by means of V.R. Tech., India make microprocessor based digital Pirani gauge to measure the vacuum from atmosphere to $10^{-3}$ mbar and penning gauge to measure the vacuum in the range of $10^{-3}$ to $10^{-7}$ mbar. The system gives an ultimate vacuum of about $1 \times 10^{-6}$ mbar. Pure argon was used as sputter gas and oxygen as reactive gas. Pure oxygen gas was admitted into the chamber through mass flow controller (Model GFC 17, Aalborg, Germany). A continuously variable dc power supply of -50 V to -1000 V with 1 A maximum current was used as a power source for sputtering. The substrate holder has been provided to heat the substrate to maximum temperature of 700°C to heat by conduction phenomenon. Temperature measurement and control is done by means of digital PID controller which works in conjunction with Iron-Constantan K-type thermocouple. The substrate holder is provided with provision of back and forth...
ration to achieve uniform coating. Before deposition of each film, the targets were pre-sputtered in pure argon atmosphere for 10 min. to remove oxide layers if any on the surface of the targets. The target to substrate distance was kept at 60 mm apart.

2.5. **Preparation of CdZnO thin films by dc reactive magnetron sputtering:**

Thin films of CdZnO were prepared from 2" Zn and Cd targets of 99.999% purity on well cleaned microscope glass substrates using dc magnetron sputtering technique. The chamber was evacuated to a base pressure of $8 \times 10^{-6}$ mbar using oil-diffusion pump backed up by rotary pump. To remove the native oxide layers, the targets were pre-sputtered for 10 min. by introducing pure argon gas into the chamber. During the depositions, the sputtering pressure was maintained constant at 0.04 – 0.06 mbar. The target to substrate distance was maintained constant at 60 mm. The CdZnO thin film properties depend on various deposition conditions. In the present study, the CdZnO thin films were deposited at various growth parameters: i) Substrate temperature, ii) Post sputter annealing temperature, iii) Oxygen flow rate and iv) Cd sputter power.

The deposited CdZnO thin films were characterized by studying their structural, smorphological, optical and electrical properties. The deposited films were irradiated with 100 MeV gold ($\text{Au}^{7+}$) and oxygen ($\text{O}^{7+}$) at Inter-University Accelerator Centre, New Delhi and studied the effect of heavy ion irradiation on the films with irradiation.

2.6. **Irradiation of CdZnO thin films:**

2.6.1. **Introduction:**

Ion beams are also used for the modification of target material [51]. In ion implantation experiments the projectile ions are implanted into a target material creating alloys or inducing defects. The target modification can be very precisely
controlled, since the number of ions in the beam per area determines the number of implanted ions, while the beam energy controls the depth profile.

SHI irradiation of insulators has long been known to create macroscopic structural modifications both in bulk and surface. Such modifications, commonly called ion tracks, may appear as craters or hillocks on the surface, which are detectable, for instance by means of atomic force microscopy [52]. Other more subtle modifications are color centers and changes in the chemical composition or binding of atoms. Such modifications can sometimes be detected by chemical etching of the surface. The damaged area, both bulk and surface, will exhibit a different etching rate compared to that of the virgin sample.

2.6.2. **SHI Irradiation:**

SHI irradiation has been done at Inter-University Accelerator Centre (IUAC) (Formerly known as Nuclear Science Centre), New Delhi. The Accelerator at IUAC is 15 UD tendem type electrostatic accelerator [53] capable of accelerating any ion from proton to uranium (Except Inert gases) to the energies ranging from 50 MeV to 200 MeV. The principle of acceleration of ions is shown in schematic below fig. 2.10.

The 15 UD Pelletron is a versatile and has vertical geometry installed in a stainless steel tank which is 26.5 m long and 5.5 m in diameter. It is filled with sulphur hexafluoride (SF$_6$) insulating gas at a pressure of about 6-7 bar. In the middle of the tank, a high voltage terminal of about 1.52 m in diameter and 3.81 m in height is provided and this terminal can be charged with the potential from 4 to 16 MeV. A potential gradient was maintained with ceramic titanium diffusion bonded accelerating tubes from high to ground voltage at the top of the tank as well as at bottom of the tank.
The negative ions produced and pre accelerated to about 250 keV by a sputter type ion source known as multi-cathode source of negative ions by cesium sputtering (MC-SNICS). The ions of different masses are analyzed by a 90° dipole magnet called injector magnet and are turned in vertically downward direction towards the terminal. On reaching the terminal, they pass through a stripper (N₂ gas) that strips the electrons from ions, thus changing them to positive ions, which are further accelerated as they proceed towards the bottom of the tank at ground potential. The final energy of the ions merging from the accelerator is given by

$$E = E_{\text{deck}} + (1 + q)V_T$$

where $V_T$ is the terminal potential in MV, $q$ is the charge state of the ion after stripping and $E_{\text{deck}}$ (few hundred of kV) is the deck potential of the MC-SNICS source. These high energy ions are analyzed in energy with the help of a 90°

**Fig. 2.10** The principle of acceleration of ions in Pelletron
bending magnet known as analyzer magnet and directed to the desired experimental beam line with the help of a multipoint switching magnet which can deflect the beam in any of the seven beam lines in beam hall-I. The whole beam line of the accelerator is in UHV. During passage of ions through accelerator beam line, the ion beam is kept centered and focused using steering magnets and quadrupole triplet magnets. The beam is visually monitored by glow on quartz and beam profile monitors (BPM). The beam current is measured by means of Faraday cups.

The accelerator beam from the Pelletron is brought to the beam hall and can be switched to anyone of the seven beam lines. Among them, one is materials science beam line, which is at 15° to right with respect to the zero degree beam line. Materials science beam line has three chambers and these are connected one after another. In high vacuum chamber, most of the irradiation and elastic recoil detection analysis experiments are performed. It is of 68 cm diameter and is made of stainless steel. The vacuum in the chamber is created by using turbo molecular pump. The vacuum during irradiation experiment was in the order of $10^{-6}$ mbar. The target ladder containing samples mounted on it is inserted in the chamber. Fig. 2.11 shows the schematic diagram of sample holder (ladder) used for swift heavy ion irradiation. A stepper motor in conjunction with suitable mechanical assembly is used to control the up and down motion of the ladder. This up and down motion can also be done from the remote data acquisition room using an electronic control system. The sample position can be aligned with respect to the ion beam by first looking at the luminescence of the beam on quartz crystal and then the-
Fig. 2.11 Schematic diagram of sample holder (Ladder) used in SHI irradiation

Sample is brought to the position of quartz by making on the screen. The position of the quartz and samples can be observed by using close circuit television (CCTV) kept in data acquisition room. There is a provision in the ladder for performing in-situ receptivity and variable temperature irradiation studies also. For irradiation, the beam is scanned in x and y-directions in the maximum area of 10 × 10 mm² with the help of magnetic scanner. The scanner ensures the uniformity of irradiation over the whole area of sample. A cylindrical enclosure of stainless steel (Suppressor) surrounds the sample ladder, which is kept at a negative potential of 120 V. This enclosure suppresses the secondary electrons coming out of sample during irradiation. An opening in the suppressor allows the ion beam to incident on the sample. The total number of the particles/charges on the sample can be estimated by the combination of the current integrator and the pulse counter from which the
irradiation fluence can be measured. Further, the fluence can also be calculated by measuring the irradiation time and by knowing the area of sample under irradiation.

**PnA (particle nanoampere) and calculation of fluence:**

PnA – Particle nanoampere can be calculated using the definition of ampere as below:

\[
1 \text{ Ampere} = \frac{1 \text{ Coulomb}}{1 \text{ Second}}
\]

\[
1 \text{ nanoampere} = 10^{-9} \left[ \frac{\text{Coulomb}}{\text{Second}} \right] \quad \text{------ (2.4)}
\]

Also,

\[
1 \text{ Coulomb} = \frac{1}{1.6 \times 10^{-19}} \text{ Charges} \quad \text{------ (2.5)}
\]

Since, Charge on the electron is \(1.6 \times 10^{-19}\) coulomb.

\[
1 \text{ nA} = 10^{-9} \left[ \frac{1}{1.6 \times 10^{-19}} \right] \text{ Charges second}^{-1} \quad \text{------ (2.6)}
\]

\[
1 \text{ nA} = 6.25 \times 10^9 \text{ Charges Second}^{-1}
\]

\[
1 \text{ PnA} = \left[ \frac{6.25 \times 10^9}{\text{Charge State of Ion}} \right] \text{ ions s}^{-1} \text{ and } \text{PnA} = \frac{\text{Beam Current}}{\text{Charge State}} \quad \text{------ (2.7)}
\]

\[
1 \text{ PnA} = \left( \frac{\text{Beam Current} \times 6.25 \times 10^9}{\text{Charge State}} \right) \text{ ions s}^{-1} \quad \text{------ (2.8)}
\]

\[
\therefore \text{Required dose (Fluence)} = \frac{\text{Time (s)} \times \text{PnA (ions s}^{-1})}{\text{Area of Irradiation (cm}^2\text{)}} \quad \text{------ (2.9)}
\]

\[
\therefore \text{Time (s)} = \frac{\text{Fluence (ions cm}^{-2}) \times \text{Area (cm}^2\text{)}}{\left( \frac{\text{PnA = Beam Current} \times 6.25 \times 10^9}{\text{Charge State}} \right) \text{ions s}^{-1}} \quad \text{------ (2.10)}
\]

**Example:** Required fluence is \(1 \times 10^{13}\) ions/cm\(^2\), measured beam current is 7 nA and the charge state is +7, then the time required to irradiate the sample area of 1 cm\(^2\) is given by

\[
\text{Time (s)} = \frac{1 \times 10^{13} \text{(ions/cm}^{-2}) \times 1 \text{(cm}^2\text{)}}{\left( \frac{7 \times 6.25 \times 10^9}{7} \right) \text{ions/s}} = 1600 \text{ sec} = 26 \text{ min. 40 sec.}
\]
Chapter II

Experimental details

The details of ion species used in the present investigations are tabulated in table 2.1. The fluence used from various ion species is in the range $1 \times 10^{11} - 1 \times 10^{13}$ ions/cm².

<table>
<thead>
<tr>
<th>Ion</th>
<th>Energy (MeV)</th>
<th>$S_e$ (keV/nm)</th>
<th>$S_n$ (keV/nm)</th>
<th>Range (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$^{7+}$</td>
<td>100</td>
<td>18.20</td>
<td>4.620</td>
<td>10.59</td>
</tr>
<tr>
<td>O$^{7+}$</td>
<td>100</td>
<td>1.242</td>
<td>0.7209</td>
<td>57.91</td>
</tr>
</tbody>
</table>

The calculation of electronic energy loss ($S_e$) and nuclear energy loss ($S_n$) is done using SRIM 2013 program [54]. It is observed that in both the cases the maximum energy deposition takes place by means of inelastic collisions (electronic energy loss-$S_e$) but not by elastic collisions (nuclear energy loss-$S_n$) by the ions having the energies in the range of few MeV to few hundreds of MeV. However, in the present studies the maximum $S_e$ in CdZnO films is observed from gold ions when compared to that of the oxygen ions.

2.7. Techniques used for the characterization:

In the present study, the characterization techniques, which have been employed to measure and evaluate the physical properties viz. film thickness, crystal structure, surface morphology, film composition, optical transmittance, optical band gap, electrical parameters of the deposited CdZnO films are described below.

2.7.1. X-ray diffraction studies:

A non-destructive X-ray diffraction is a fundamental characterization technique for the identification of the lattice structure and phase identification [55]. This technique is applicable to solids (powders) or films on substrate. It is useful in providing wide variety of information like crystallinity of the material, lattice
parameters, phase, average crystallite/grain size, dislocation density, stress etc. In the present studies, glancing angle XRD is used to analyze the synthesized CdZnO samples. The purpose of the GAXRD is to limit the penetration of X-rays to few nanometers from the surface i.e. the diffraction pattern thus obtained is only by the contribution of film and not by the substrate. The detailed technical specifications found elsewhere [56].

The basic law involved in the diffraction method of structural analysis is the Bragg’s law. When the monochromatic X-rays impinge upon the atoms in a crystal lattice, each atom acts as a source of scattering. The crystal lattice acts as series of parallel reflecting planes. The intensity of the reflected beam at certain angles becomes maximum when the path difference between two reflected rays from two different planes is an integral multiple of $\lambda$. This statement is called Bragg’s law and is given by the relation,

$$2d\sin\theta = n\lambda \quad \text{(2.11)}$$

where $n$ is the order of diffraction, $\lambda$ is the wavelength of X-rays, $d$ is the inter-planar spacing and $\theta$ is the glancing angle. Using $d$ values, the set of lattice planes $(hkl)$ can be identified and the lattice parameters are evaluated. For Hexagonal structure the lattice planes $(hkl)$ can be identified using the relation

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{1^2}{c^2} \quad \text{(2.12)}$$

where $a$ and $c$ are lattice parameters.

In the present investigation, the X-ray Diffraction (XRD) data has been collected at room temperature using the Bruker AXS D8 Advance Diffractometer (figure 2.12) with Cu $K_\alpha$ radiation ($\lambda=0.15054$ nm). The diffractometer works in 0-0 Bragg-Brentano geometry which is very useful for dealing with different types of samples.
X-ray Diffraction studies give the diffraction patterns of the samples which are compared with the standard powder diffraction films published by the international centre for diffraction data (ICDD). The average crystallite size of the films (D) is calculated using Debye-Scherrer formula,

\[ D = \frac{0.94\lambda}{\beta \cos \theta} \]  

\[ \text{(2.13)} \]

where \( \beta \) is the Full width at half maximum (FWHM). The lattice period \( c \) (c-axis constant) for the hexagonal crystal can be calculated by using Bragg’s law:

\[ c = \frac{\lambda}{\sin \theta} \]  

\[ \text{(2.14)} \]

where \( \lambda \) is the wavelength of X-ray radiation (0.15054 nm), \( \theta \) is the Bragg’s angle of the dominant peak (degrees).

**Fig. 2.12** Bruker AXS D8 Advance Diffractometer (IUAC, New Delhi).

The number of defects in the films can be determined by calculating dislocation density \( (\delta) \) using the following relation [57]:
\[ \delta = \frac{1}{D^2} \] 

where \( D \) is the average crystallite/grain size (nm).

The variation of \( c \)-axis constant is inherently related to the presence of stress in the films. Including the thermal expansion coefficients of CdZnO (\( \alpha_{\text{CdZnO}} = 6.1 \times 10^{-6} \text{ K}^{-1} \) [58]) and the glass substrate (\( \alpha_{\text{glass}} = 9 \times 10^{-6} \text{ K}^{-1} \) [59]), the stress (\( \sigma \)) in the films [60, 61] can be derived using the following relation:

\[
\text{Stress} (\sigma) = \frac{2c_{13}^2 - c_{33}(c_{11} + c_{12})}{2c_{13}} \times \left[ \frac{c_{\text{film}} - c_{\text{bulk}}}{c_{\text{bulk}}} + \left( \frac{\alpha_{\text{CdZnO}} - \alpha_{\text{glass}}}{\alpha_{\text{glass}}} \right) \Delta T \right] \tag{2.16}
\]

where \( \Delta T \) is difference of the substrate temperature and the room temperature, \( c_{\text{film}} \) represents the calculated \( c \)-axis length of the film, and \( c_{\text{bulk}} = 0.52054 \text{ nm} \), the values for elastic constants used are: \( c_{11} = 208.8 \), \( c_{33} = 213.8 \), \( c_{12} = 119.7 \) and \( c_{13} = 104.2 \text{ GPa} \) [62]. The strain in the films in the direction of the \( c \)-axis can be determined by XRD as

\[
\varepsilon = \frac{c_{\text{film}} - c_{\text{bulk}}}{C_{\text{bulk}}} \tag{2.17}
\]

**2.7.2. Atomic force microscopy:**

The AFM probes the surface of the sample with a sharp tip, a couple of microns long often less than 100 Å in diameter. The tip is located at the free end of a cantilever, which is 100 to 200 μm long. The forces between the tip and sample surface cause the cantilever to bend or deflect. A detector measures the cantilever deflection as tip is scanned over the sample or the sample is scanned under the tip. The measured cantilever deflection allows the computer to generate a map or surface topography.

Several forces typically contribute to the deflection of an AFM cantilever. AFM operates by measuring the attractive or repulsive forces between a tip and the sample. The forces most commonly associated with atomic force microscopy are
inter-atomic force called the Van der Waals force. The dependence of the Van der Waals force upon the distance between the tip and the sample is shown in figure 2.13. The two distance regimes are labeled in the figure (a) the contact regime and (b) non-contact regime.

Fig. 2.13 Inter-atomic force versus distance curve for the operation of AFM

In the contact regime, the cantilever is held at a distance less than few angstroms from the sample surface, and the inter-atomic force between the cantilever and the sample is repulsive. In the non-contact regime, the cantilever is held at a distance of the order of tens to hundred of angstroms from the sample surface, and the inter-atomic force between the cantilever and sample is attractive. Figure 2.14 shows schematic diagram of AFM [62, 63].

Fig. 2.14 Schematic diagram of AFM
In principle, AFM resembles the record player as well as the surface profilometer. However, AFM incorporates a number of refinements that enable it to achieve atomic–scale resolution: Sensitive detection, flexible cantilever, sharp tips, high-resolution tip sample positioning and Force feedback.

2.7.3. **Field emission-scanning electron microscopy:**

The scanning electron microscopy is a versatile, non-destructive technique that reveals detailed information about the morphology and the composition of natural and manufactured materials at higher magnification, higher resolution and depth of focus as compared to an optical microscope. Researchers in biology, chemistry and physics apply this technique to observe structures that may be as small as 1 nanometer (= billion of a millimeter). The FESEM may be employed for example to study organelles and DNA material in cells, synthetic polymers, and coatings on microchips.

**Principle:** FESEM is a microscope that works with electrons (particles with a negative charge) instead of light. These electrons are liberated by a field emission source. The object is scanned by electrons according to a zig-zag pattern. In standard electron microscopes electrons are mostly generated by heating a tungsten filament by means of a current to a temperature of about 2800°C. Sometimes electrons are produced by a crystal of lanthanum hexaboride (LaB$_6$) that is mounted on a tungsten filament. This modification results in a higher electron density in the beam and a better resolution than with the conventional device. In a field emission (FE) scanning electron microscope no heating but a so-called "cold" source is employed. An extremely thin and sharp tungsten needle (tip diameter $10^{-7}–10^{-8}$ m) acts as a cathode in front of a primary and secondary anode. The voltage between cathode and anode is in the order of magnitude of 0.5 to 30 KV. Because the
electron beam produced by the FE source is about 1000 times smaller than in a standard microscope, the image quality is markedly better. As field emission necessitates an extreme vacuum ($10^{-8}$ Torr) in the column of the microscope, a device is present that regularly decontaminates the electron source by a current flash. In contrast to a conventional tungsten filament, a FE tip last theoretically for a lifetime, provided the vacuum is maintained stable.

FESEM: MIRA II LMH from TESCAN, with a resolution of 1.5 nm at 30 kV has been installed to boost research activities in nanomaterials, in a project funded under Nano Initiative program of Department of Science and Technology (figure. 2.15). It has a secondary electron (SE) and a backscattered electron (BSE) detector for imaging. An energy dispersive X ray detector INCA PentaFET3 with 133 keV resolution from OXFORD has also been installed in this system for elemental analysis.

Fig. 2.15 FESEM with EDX attachment (IUAC)
2.7.4. **Energy dispersive analysis by X-rays:**

In EDX technique a sample is made the target in an X-ray tube and is bombarded with electrons of suitable energy, it emits characteristics X-rays. This is the basis of a method of chemical analysis. The emitted X-rays are analyzed in an X-ray spectrometer and the elements present in the sample are qualitatively identified by their characteristics wavelengths. For compositions greater than or about 1% and elements separated by few atomic numbers, energy dispersion analysis is very useful because the intensities are increased about 100-Fold [64]. The resolution however, of an energy dispersion instruments is as much as 50 times less than the wavelength dispersion spectrometer using a crystal; thus overlapping of lines from nearby elements may occur. If a sample is irradiated with X-rays of sufficiently high energy, it will emit fluorescent radiation. This radiation may be analyzed in an X-ray spectrometer and the elements present in the sample can be identified by their characteristics wavelengths. Study of thin films, ferrites, composites, biological samples and pharmaceutical samples are the common application areas.

2.7.5. **UV-vis-NIR Spectrophotometer:**

Thin film optical properties study is of most important for variety of applications. This deals primarily with reflectance \( R \), transmittance \( T \) and absorbance \( A \) properties and their relation with the optical constants of the film. The optical absorption coefficient \( \alpha \) in the absorption region was determined using the relation [65],

\[
\alpha = \frac{1}{d} \ln \left( \frac{1}{T} \right) \tag{2.18}
\]

The optical constants such as refractive index, extinction coefficient, optical band gap, and optical transmittance can be studied by UV-visible
spectrophotometer. For crystallite materials, the transition of electrons from valence band to conduction band can be grouped in to direct and indirect process [66]. In direct inter band optical transitions, the value of wave vector $k$ for elements remains unchanged in $E$-$k$ space and momentum also does not change, whereas in indirect inter band transition, the wave vector $k$ for electrons changes in the $E$-$k$ space. Thus, vertical transitions are important when the valence and conduction bands extreme are located at the same point in the Brillouin zone. For indirect transition, the band extreme differs in their positions in $E$-$k$ space. It is possible to differentiate the nature of optical transition as direct allowed or direct forbidden by using classical relation:

$$\alpha = \left[A(h\nu - E_g)^n\right]/h\nu$$

where, $E_g$ is the separation between bottom of the conduction band and top of the valence band, $h\nu$ is the photon energy and $n$ is constant. For allowed direct transition, $n = 1/2$ and allowed indirect transition, $n = 2$. Thus if the plot of $(ah\nu)^2$ against $h\nu$ is linear, the transition is direct allowed. Band gap energy $E_g$ has been determined by extrapolating the linear portion of the curve on to the energy axis at $\alpha = 0$. Though the optical band gap, nature of transition, transmission etc could be easily obtained from optical absorption, the reflectance $R$ is assumed to be zero and the equation depends only on classical approach.

The optical transmittance and absorbance of the films deposited on to glass substrates measured using a spectrophotometer (Hitachi Japan, Model No. 330). The light emitted from the source (deuterium or tungsten lamp) is passed through the two grating monochromators for obtaining monochromatic beam and then it is splitted in to two beams. After passing through the sample and reference compartment, the monochromatic beams are converged and then converted in to an
electrical signal by a detector or photomultiplier tube. The detected signal is
digitized by a 16 bit A/D converter. The wavelength range used was 200 nm to 800
nm. The internal block diagram is shown in the fig. 2.16.

If the sample compound does not absorb light of a given wavelength I
becomes equal to I₀. However, if the sample compound absorbs light then I is less
than I₀, and this difference may be plotted against wavelength. Absorption may be
presented as transmittance \( T = I/I₀ \) or absorbance \( A = \log I₀/I \). If no absorption
has occurred, \( T = 1.0 \) and \( A = 0 \). Most spectrometers display absorbance on the
vertical axis, and the commonly observed range is from 0 (100 % transmittance) to
2 (1% transmittance).

![Schematic diagram of ultraviolet-visible Spectrometer](image)

**Fig. 2.16** Schematic diagram of ultraviolet-visible Spectrometer

**i. Film Thickness measurement:**

The thickness of the film was measured by using the well-known Tolansky
method [67]. This method is a multiple-beam interference technique used for the
measurement of the thickness of the thin films deposited on the flat, smooth and
transparent substrate. A sharp step is formed between film and the masked region
of the substrate at the time of deposition (etching to make it highly reflecting
layer). Using the highly reflecting layer as one surface of an interferometer and viewing the multiple beam fringes by reflection, the height of the step can be measured. This step height gives the thickness of the films.

**ii. Refractive index and Extinction coefficient measurement:**

Refractive index is one of the important optical constant in optically transparent thin film. In this present work, two methods have been used to measure the refractive index of thin spectrophotometric method. This method is based on the spectrometric results, by measuring the simultaneous absorption and transmittance of thin film at eye sensitive 621 nm wavelength, the reflectance has been calculated by using relation,

\[
\text{Transmittance} + \text{Absorption} + \text{Reflectance} = 1 \quad ---- (2.20)
\]

The refractive index \(n\) of thin films calculated by using the following formula:

\[
n = \frac{n_s^2 T_f + n_s \left(1 + \sqrt{R_f}\right)^2}{T_f + n_s \left(1 - \sqrt{R_f}\right)} \quad ---- (2.21)
\]

where \(n = \) refractive index of the film \(n_s = \) refractive index of the substrate \(T_f = \) transmittance of the film and \(R_f = \) reflectance of the film. If the transmittance profile is in the form of sin waves, the refractive index can be calculated from the following formula:

\[
n = \sqrt{N + \sqrt{(N^2 + n_0^2 n_1^2)}} \quad ---- (2.22)
\]

where \(n_0\) is the refractive index of air, \(n_1\) is the refractive index of the substrate (glass=1.5) and

\[
N = \frac{(n_0^2 + n_1^2)}{2 + 2n_0 n_1 (T_{\text{max}} - T_{\text{min}}) / T_{\text{max}} T_{\text{min}}} \quad ---- (2.23)
\]

where \(T_{\text{max}}\) and \(T_{\text{min}}\) are the upper and lower extreme transmittance values for the given wavelength obtained from the envelope curves. By using the absorption coefficients, the extinction coefficient \((k)\) of the film can be determined using the following relation:
\[ k = \frac{\alpha \lambda}{4\pi} \] \hspace{1cm} ---- (2.24)

2.7.6. Hall measurement system:

The Hall Effect was discovered by Edwin Hall in 1879 and permits the determination of mobility and carrier properties within a sample [68, 69]. Hall voltage is denoted by \( V_H \) and can be described as the voltage upon a long thin sample of length \( a \), where a current \( I \) is driven through the long axis and a magnetic field \( B \) is applied perpendicular to the sample. Denoted by the balance of the Lorentz force and the electric field force induced due to the Hall voltage, we are able to comprehend the Hall voltage for an n-type sample when integrating over the transverse field \( E_H \).

\[ \frac{B}{IB} q d V_H = \frac{1}{nq d} IB \quad \text{------- (2.25)} \]

where \( V_H \) is the Hall voltage, \( B \) is the magnetic field, \( q \) is the charge of an electron, \( n \) is the charge carrier density and \( d \) is the thickness of the sample. From this equation the term \((-1/nq)\) is known as the Hall constant \( R_H \) for a given sample, from which the sign dictates whether the measured sample is n-type or p-type. The Hall voltage equation can therefore be rewritten as shown in equation:

\[ V_H = R_H \frac{1}{d} IB \quad \text{------- (2.26)} \]

Following this, when the Hall constant is determined the carrier concentration may be calculated n-type and p-type semiconductors

\[ n = \frac{1}{R_H q} \quad \text{------- (2.27)} \]

\[ p = \frac{1}{R_H q} \quad \text{------- (2.28)} \]

The mobility and resistivity of the films from the Hall measurement system can be calculated by using the given formula

\[ \mu = \sigma R_H \quad \text{------- (2.29)} \]
where $\mu$ is the mobility of charge carriers, $\sigma$ is the conductivity, and $R_H$ is the Hall coefficient. The mean free path ($l$) is calculated using a sufficiently degenerate gal model [70, 71] given by

$$l = (3\pi^2)^{1/3} \left( \frac{\eta}{e^2} \right) \rho^{-1} n^{-2/3} \quad \text{(2.30)}$$

where $\rho$ and $n$ represents the resistivity and carrier concentration, respectively.

i. **The Van der Pauw technique:**

A Hall measurement system using Van der Pauw setup [72, 73] is used in the experiments in this dissertation. As shown in Fig. 2.17, a square sample with metal contacts at each corner of the sample is used in the measurement. Magnetic field $B$ is applied perpendicular to the sample surface. Current $I$ is applied from one contact to the other on the diagnostic direction. Hall voltage $V_H$ is measured across the other two contacts on the sample. Several practical considerations must be accounted for during these measurements:

- Ohmic contact quality and size
- Sample uniformity and thickness accuracy
- Thermomagnetic effects
- Photoconductive and photovoltaic effects

![Fig. 2.17 Van der Paul Hall effect setup](image_url)
Chapter-II  Experimental details

References:


[56]. https://www.bruker.com/