Chapter 2

Thin Film Fabrication and Characterization Techniques
2. THIN FILM FABRICATION AND CHARACTERIZATION TECHNIQUES

The role of individual thin film is vital in any multilayered thin film device structure. The defect free thin film is the prior criteria for healthier performance of the thin film device. This chapter discusses the thin film deposition methods in brief. Thin film characterization techniques used to investigate the structural properties viz. X-ray diffraction (XRD), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), and Atomic force microscopy (AFM) are also discussed. The optical characterization technique utilized to study the transmission and reflection of the grown thin films. In the electrical measurements of thin films, Van der Pauw method, four-point probe method, and Hall-effect are elaborated.

2.1 THIN FILM FABRICATION TECHNIQUES

Methods of making or depositing the thin film can be divided into two parts: one is physical vapor deposition (PVD) and other one is chemical vapor deposition (CVD). Thermal or flash evaporation (resistive heating), e-beam evaporation, sputtering are the examples for PVD, while Low Pressure CVD, Plasma Enhanced CVD (PECVD), Laser Enhanced CVD (LECVD), Metal-organic CVD (MOCVD) are the examples of CVD. Depending upon the application the vacuum system is attached with the deposition method. In the present thesis we are using thermal evaporation, flash evaporation, and RF magnetron sputtering. These different PVD techniques are described in the subsequent sections.

In PVDs the atoms or molecules, of the evaporable material, energized from a thermal vaporization source or from the ionization process, reach the substrate. Successful vapor transport process from the source to substrate is done by reducing the number of gas collisions, and enabling high energy particles to be used as part of the deposition process. This course of action requires a good vacuum near to $10^{-6}$ mbar. A vacuum could be described as where within an enclosed volume there is less gas particle per unit volume than is present in a similar volume in the atmosphere surrounding the enclosed volume. The word vacuum is derived from the Latin word “vacua” meaning empty. If we empty the chamber of gas, we produce a vacuum. This can be used for our advantage. Less gas particle in particular area gives a less obstacle for atoms or molecules of the material in the vapor transport process from source to substrate. This physical process is known as a “mean free path”. In the simple manner the mean free path is the average distance between the successive
collisions of vaporized material with the present gas atoms. The length of the path depends on the molecular diameter of the gas particle, the density of molecules, and their average velocity. The vaporized phase of the material collected on to the substrate, this collection of the material is named as a thin film. The process of making the thin film can be divided into few steps namely, thermal accommodation, binding, surface diffusion, nucleation island growth with coalescence, and continued film growth.

In the thermal accommodation process impinging atoms must lose enough energy thermally to stay on surface. More then one atoms attach with each other by two types of surface bond. One is physisorption (physical adsorption) in which the Van der Waals type the attachment is observed between the atoms. This type of the bonds is weak bonds. The second one is chemisorption (chemical adsorption) deals with the chemical bonds between the atoms and they are strong bonds. Within or after the binding process the atoms are move around on the surface. The process of an atom moving around on the surface is known as surface diffusion. The higher the energy the atoms arrive with on the surface the more and faster they move around on the surface. The atoms continue to move until they reach a position that minimizes the total energy.

As more atoms arrive, they undergo the same process, attached with the atoms which are already sticking to the surface and so the nucleated particles will grow. Once the nuclei reach a critical size, it gets stable and fixed. There are various mechanisms for the further growth of the nuclei shown in Fig. 2.1 [33]. Van der Merwe mechanism describes the method where the atoms cover the whole surface before a second layer is grown. If the nuclei grow as hemispheres and a thin film is formed once the hemispheres have grown large enough to touch each other, then it is referred to as the Volmer-Weber mechanism. If the growth process is a combination of the two by first covering the surface and then growing by hemispheres, it is referred to as the Stranski-Krastanov mechanism. In roll coating onto polymer surfaces, the growth will be by the Volmer-Weber mechanism.

![Fig. 2.1 A schematic diagram for the different vacuum based growth techniques of thin film.](image)

In all the above listed mechanism the substrate roughness will lead to preferential nucleation. Nucleation will start in the valleys between peaks. Hence, defects in the surface
can generate defects in the subsequent coating. Figure 2.2 describes the surface dependency during the nucleation process.

![Substrate dependence nucleation of atom and finally the effect of it on thin film growth.](image)

As the randomly positioned nuclei increase in size into islands, there will be some that come into close proximity. Once the spacing between any two nuclei or islands gets to within a critical distance, they will move toward each other and coalesce into a single entity (Fig. 2.3). With the arrival of more atoms, the nuclei and islands continue to grow and coalescence continues. When larger islands coalesce, the area they move from is denuded of material and so new nuclei will form and grow. With the continued growth, there will be coalescence of several nuclei and islands into more complex shapes. Eventually, this will result in a network of interconnected islands.

![Schematic of coalescence of a couple of nuclei of thin film.](image)
The network will expand and undergo further coalescence, increasing the conduction paths for more efficient conduction and thus reducing the resistance. The surface will become more completely covered apart from some isolated holes as shown in Fig. 2.4. Depending on the conditions, the coating might be quite thick before the last of the holes is filled in.

![Diagram showing different stages of nucleation and initial growth of thin film](image)

**Fig. 2.4 Schematic showing the different stages of nucleation and initial growth of thin film.**

Various kind of deposition techniques were used in general for making the thin film of a particular material. That is highly depends on the melting or sublimation temperature of the material. In the present work for the deposition of CIGS powder and CdS powder, flash and thermal evaporation was used. For the deposition of Molybdenum and intrinsic as well as Al doped ZnO, RF magnetron sputtering was used. Thermal evaporation, flash evaporation, and RF magnetron sputtering are discussed in details in the next section.

**Substrate preparation**

Thin film growth and adhesion is fundamentally related to the substrate surface conditions. It is therefore crucial to thoroughly clean the substrate before the deposition process. In industry this is often done by using the etching chemicals or plasma etching. Here we are used the soda lime glass substrate. To remove the impurities from the glass surface first we placed it in the 5 % dilute \( \text{H}_2\text{O}_2 \) solution. Afterward, a hot bath of acetone, trichloroethylene and methanol is provides followed by drying it by nitrogen flow. Dried clean glass substrate is kept in clean environment at \( \sim 40 \, ^\circ\text{C} \) temperature before used it for the evaporation.
2.1.1 Thermal and Flash Evaporation

Thermal vaporization requires that the surface, and generally, a significant volume of the material must be heated to a temperature where the material gets melt and an appreciable vapor pressure built up. A common technique for melting or evaporating/sublimating the material was resistive heating. Different types of evaporation sources are used for the resistive heating [34].

![Diagram of vacuum chamber for thermal and flash evaporation](image)

Fig. 2.5 Schematic of the specially designed vacuum chamber for thermal and flash evaporation which has multiple substrates holder with rotation facility.

Fig. 2.5 shows a typical schematic of thermal and flash evaporation setup. The thickness of the thin film is measured by Quartz crystal thickness monitor. The substrate temperature is provided by the 1000 W halogen tube, placed just above the substrate holder. The substrate holder is made such a way that in a single evacuation operation, multiple number of the thin film can be made.

By observing the setup as shown in Fig. 2.5, there is a minor difference between thermal and flash evaporation. In the thermal evaporation the evaporation source is preloaded with the material, but in the flash evaporation technique there is a separate container which is loaded with the material. At the time of the deposition the material is fall on the evaporation
source slowly and gets vaporized. Molybdenum Baffled Box type evaporation source is used for the deposition CdS and CIGS material. Flash evaporation technique is more useful for the evaporation of the ternary or quaternary alloys and compound, which is made up of elements having a different vapor pressure and melting temperature values. Because of the instant vaporization of the material the spiting of the material is very less. While in the thermal evaporation method, only single elements or binary alloys and compounds can be evaporated.

**Post-deposition annealing**

To increase the stability, compactness and grain size of the thermal or flash evaporated thin film, there is a need for rapid post-annealing. In our study a specially designed rapid thermal annealing (RTA) furnace was used. The schematic and photograph of RTA furnace, is shown in the Fig. 2.6.

![Fig. 2.6 Schematic of the vacuum based RTA furnace.](image)

The quartz tube is placed in a circular cylinder with circularly arranged six halogen tubes (1000 W each). One end of the tube is connected to the vacuum system and the in other one there is an arrangement for the sample loading/unloading and thermocouple. The thermocouple and the halogen tube are connected to the furnace controller, which consists of PR502 (Selec Controls, Mumbai, India) programmable temperature controller and locally made solid state relay (SSR). Gas inlet point is available for providing the reactive annealing process.

**2.1.2 RF Magnetron Sputtering**

Sputtering is a widely used and well known technique for the erosion of any kind of surfaces and the preparing thin films of them. Sputtering is mainly used for patterning the
semiconductor wafers, cleaning surfaces, depth-profiling measurement, and a number of applications [35].

The simplest kind of plasma device, a diode sputtering, is simply an anode and a cathode arrangement having a specific distance between them inside a vacuum system. Under the right conditions, with enough voltage across the electrodes and the appropriate gas pressure, the gas will breakdown into a plasma discharge. In this discharge, the potential of the plasma is spatially uniform, slightly higher than the potential of anode. Near the cathode, there is a very large electric field. Ions are accelerated rapidly across the electric field and strike the cathode. As part of this collision (which can cause sputtering), occasional electrons, known as secondary electrons, are emitted from the surface. These electrons are accelerated back across the electric field and gain significant energy. This energy can be used, through the collisions with gas atoms, to form more ions to sustain the discharge process. The secondary electrons are the primary source of energy to the plasma discharge, and each secondary electron must generate a significant number of ions.

Fig. 2.7 Schematic of RF magnetron sputtering system with water cooled arrangement below the cathode.
In the case of the insulating material there is no plasma because of the least generation of secondary electrons from the insulating surface. Radio frequency (RF) sputtering gave the solution for that. The cathode and anode are electrically reversed in RF sputtering for the elimination of charges that builds-up on an insulating surface by providing the equal number of ions and electrons. This allows insulators to be sputtered. Due to the cyclic motion of the generated electrons while sputtering of insulator by RF, that makes it complex and highly system dependent. Confining the generated secondary electrons, i.e. plasma, at particular area by using the magnets resolve this problem. The schematic of the RF magnetron sputtering system is shown in Fig. 2.7.

A magnetron uses a static magnetic field that is configuring at the cathode plate. The magnetic field is located parallel to the cathode surface. Secondary electrons emitted from the cathode due to the ion bombardment are constrained by the magnetic field to move further in a direction perpendicular to both the electric field (normal to the surface) and the magnetic field. This is known as an \( E \times B \) drift, which is also the basis for the Hall Effect. This drift causes electrons to move parallel to the cathode surface in a direction 90 degrees away from the magnetic field. We used RF power supply of 600 W from HÜTTINGER Elektronik, Germany and circular magnetron cathode from Angstrom Sciences Inc, USA.

2.2 CHARACTERIZATION TECHNIQUES

2.2.1 X-ray Diffraction

X-ray diffraction (XRD) is a powerful non-destructive diagnostic tool in analyzing the crystalline phases of thin-films and determining the structural properties of these phases such as the preferred orientation and average grain size. X-ray diffractometry (0-2θ scan geometry) using a Bruker D8 advance with Cu Kα radiation (\( \lambda = 1.540562 \) Å) was used in this thesis. The machine was typically operated at a voltage of 30 kV and current 30 mA. A standard setting for continuous scans is at an angular speed of 1° min\(^{-1}\) and a step size of 0.02° s\(^{-1}\) in a 2θ range of 0° - 100°. Schematic of X-ray diffractometer and the diffracted X-ray beam from the lattice spacing is show in Fig. 2.8 (a) and (b) respectively.

**Principle of 0-2θ scans**

A real three-dimensional crystal consists of many sets of atomic planes. These atomic layers are spaced a distance (d) and are named as d-spacing. An atomic plane can be distinguished by its miller indices (hkl), and the d-spaces between (hkl) planes denoted by \( d_{hkl} \). When X-ray beams irradiate the sample surface at certain angle of incidence, these planes of atoms scattered the incident X-rays beam. There is a constructive interference from specular
reflectance of X-rays at particular values of d-spacing and the angle of incidence $\theta_{hkl}$ onto the (hkl) planes, resulting in a diffraction peak. The condition of the constructive interference is given by the Bragg law [36]:

$$n_i \lambda = 2d_{hkl} \sin \theta_{hkl}$$  \hspace{1cm} (2.1)

Where the integer $n_i$ is known as the order of the reflection, and $\lambda$ is the X-ray wavelength. X-ray diffractometer is based on the Bragg Equation 2.1. For diffraction to be observed, the angle between the surface of the sample and the incident X-rays must be at the Bragg angle $\theta_{hkl}$, and the reflected intensity is measured by detector as a function of $2\theta_{hkl}$. In this case, X-rays are incident on the samples over a range of angles $\theta$, while reflections are detected over the range of angles $2\theta$. This XRD scan mode is known commonly as the $\theta$-2$\theta$ scans. Figure 2.8 (a) shows a schematic representation of X-ray diffractometer. Polycrystalline thin-films consist of many grains distributed in various orientations. The diffraction occurs from any grain or particles must follow the Bragg law.

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

**Fig. 2.8** Schematic of X-ray diffractometer (a) and interaction between atomic places having a finite d-spacing of material and X-ray beam (b).
The most random distribution of orientations occurs in powder samples consisting of many small crystallites with random orientations. As a result, the powder diffraction pattern can be taken as a reference for all possible diffraction peaks. In the following Chapters, diffraction data from the Joint Committee on Powder Diffraction Standards (JCPDS) are used to determine their structural properties.

**Determination of average crystallite size**

The width of diffraction peak, in a 0-2θ scan, is related to the average crystallite size of the crystals present in the sample. Under an ideal diffraction condition, namely a perfect infinitely thick crystal and an incident beam of parallel monochromatic radiation, XRD peaks become narrow lines located at the Bragg angles. The infinite number of parallel atomic planes leads to the destructive interference and complete cancellation of scattered X-rays over all angles, except for the Bragg angles. This is because an X-ray reflected at the surface can always be cancelled by an X-ray reflected from a plane deeper in the crystal, which happens to be exactly out of phase due to the additional path length. However, if the crystal is so thin that the deeper atomic planes do not exist, then there will be incomplete cancellation of scattered X-rays, leading to broader XRD lines. The incomplete cancellation of scattered X-rays can also be observed when the sample itself is a polycrystalline. This broadening of the diffraction peak helps to determine the average crystalline size (D). Scherrer's formula [36] is used to calculate it, and is given by,

\[
D = \frac{k\lambda}{\Delta(2\theta) \cos \theta}
\]

(2.2)

where \(\lambda\) is the X-ray wavelength, and \(\Delta(2\theta)\) is the FWHM in radians, \(\theta\) is the peak position in degrees. \(k\) is a constant close to 1. The size \(D\) is effectively an average coherence length of the crystal structure. It is not necessarily a measured size of an entire grain since defects, such as dislocations in the lattice structure, may divide each grain into sub-grains, or crystallites, and result in a value of \(D\), which is far smaller than the average grain dimensions measured by transmission electron microscopy (TEM) or Scanning electron microscopy (SEM).

**2.2.2 Electron Microscopy**

Beyond crystalline phases of thin-films, the surface topography and morphology, including grain size and shape, existence of compounds, evidence of film voids, micro-cracking or lack of adhesion, etc., are prior observation. In addition to that, somewhat more difficult to obtain are the cross-sectional views of multilayer structures where interfacial regions, substrate interactions, and geometry and perfection of electronic devices with associated conducting
and insulating layers may be observed using the electron microscopy. The electron microscopy is based on the scanning of the secondary electrons generated from the sample surface, called a scanning electron microscopy (SEM). Chemical or elemental analysis of the sample can also be examined by just attaching extra X-ray detector with the SEM equipment. It works upon dispersion of X-ray produced from the atoms of the sample, so called as energy dispersive analysis of X-ray (EDS). Most of the latest SEM equipments now have an extra attachment for the EDS analysis.

**SEM and EDS Analyses**

The scanning electron microscope is the versatile tool for the observation of the micron size elements and surface of specified objects. The capabilities of surface-analysis instruments, especially spatial resolution, sample handling and treatment, speed of data acquisition, and data processing and analysis have been greatly enhanced during the past three decades. The applications of these instruments have now advanced from research and development to problem solving, failure analysis, and quality control and the instruments have become more reliable.

An electron microscope uses an electron beam (e-beam) to produce a magnified image of the sample. The three principal electron microscopes are: scanning, transmission, and emission. In the scanning and transmission electron microscope, an electron beam incident on the sample produces an image while in the field-emission microscope the specimen itself is the source of electrons. A scanning electron microscope consists of an electron gun, a lens system, scanning coils, an electron collector, and a cathode ray display tube (CRT). The electron energy is typically 10 - 30 keV for most samples, but for insulating samples the energy can be as low as several hundred eV. The use of electrons has two main advantages over optical microscopes: much larger magnifications are possible since electron wavelengths are much smaller than photon wavelengths and the depth of field is much higher. The basic model for the scanning electron microscope is shown in Fig. 29

When an electron beam interacts with the sample, it gets absorbed, reflected, or transmitted and, may generate light, X-ray or electron (Backscattered, secondary). Typical depth of the electron beam in near to 1 μm. The energies produced from electron beam interaction with the sample give a wealth of information about the surface composition, and the physical structure of a sample. Electron beam microscope consists of an electron gun, a lens system, scanning coils, an electron collector, and a cathode ray display tube.
SEM can produce magnified image of the sample to study the surface topology using focused electron beam. The image in SEM is produced by detecting the secondary and/or backscattered electrons from the sample surface. The final image is created by scanning the sample in XY direction and collecting the number of electrons emitted from each spot on the sample simultaneously. The change in the contrast of image is directly related to the surface topology of the sample.

EDS provide elemental identification and quantitative compositional information by analyzing X-rays emitted by the sample when it interacts with an electron beam. The electron beam removes an inner shell electron from the sample, which cause a higher energy electron
to fill the shell and release energy as characteristic X-rays. All elements except hydrogen and helium can be detected but Sodium (Na) window in front of the detector can absorb low-energy X-rays so, it can not detect the element having the atomic number less than 11 (Na). EDS gives a quantitative analysis of elemental composition within a sampling depth of typically 0.5 to 5 nm, etching of the sample with the help of sputtering provides depth information.

**TEM analysis**

Lastly, and most complex of all, are diffraction patterns, the crystallographic information, and the high-resolution lattice images of both plain-view and transverse film sections. For that the TEM is required for these applications.

In principle a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen material as it passes through, shown in Fig. 2.10, an image is formed by the interaction process of the electrons of the specimen, transmitted through the specimen. The transmitted electrons collected on to the fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera. The image is magnified by magnetic lenses and focused onto an imaging device.

**Electron beam**

Fig. 2.10 Schematic diagram of TEM analysis, diffraction from the thin film sample collected on the photographic plate or a CCD camera.

TEMs have an imaging power with a significantly higher resolution than light microscopes, owing to the small de-Broglie wavelength of electrons. This enables the
instrument's user to examine fine detail - even as small as a single column or a raw of atoms, which is tens of thousands times smaller than the smallest resolvable object in a light microscope. TEM is one of the major analytical methods in the scientific field, in both physical and biological science. There is an interesting distinction between the TEM and SEM. The former is a true microscope in that all image information is acquired simultaneously or in parallel. In the SEM, however, only a small portion of the total image is probed at any instant, and the image builds up serially by scanning the probe.

2.2.3 AFM Analysis

The atomic force microscope is a type of scanned-proximity probe microscopes. All of these microscopes work by measuring a local property – such as height, optical absorption, or magnetism – with a probe or “tip” placed very close to the sample [37]. The small probe-sample separation (on the order of the instrument’s resolution) makes it possible to take measurements over a small area. The AFM probe having a very sharp tip, less than 10 nm diameters, is at the end of a small cantilever beam. The schematic of the AFM operation is shown in Fig. 2.11. A piezoelectric scanner tube is used for scanning the probe across a selected area of the sample surface. The Inter-atomic forces between the sample surface and the probe tip cause the cantilever to deflect as per the sample’s surface topography (or other properties) changes. Depending upon the reflected laser light from the cantilever, a data of the laser position on the four-quadrant photo-detector is fed to a computer, which generates a map of topography and/or other properties of interest. The sample areas maximum about 100 μm square to less than 100 nm square can be imaged. Various modes are available to operate the AFM.

**Contact Mode AFM:** The AFM probe is scanned at a constant force between the probe and the sample surface to obtain topographical map. When the probe cantilever is deflected by sample surface topography, the scanner adjusts the position of the probe to restore the original cantilever deflection. Lateral resolution of <1 nm and height resolution of <1 Å can be obtained.

**Intermittent Contact (Tapping Mode) AFM:** In this mode, the probe cantilever is oscillated at or near its resonant frequency. The oscillating probe tip is then scanned at a height where it barely touches or “taps” the sample surface. The system monitors the probe position and vibrational amplitude to obtain topographical and other property information. Accurate topographical information can be obtained even for very fragile surfaces. Optimum resolution is about 50 Å lateral and <1 Å height.
Fig. 2.11 Schematic diagram of AFM analysis. The deviations in the laser beam, due to the surface of the sample, imagine using the 4-quadrant position sensitive photo detector.

**Magnetic Force Microscopy:** The local variations in the magnetic forces at the sample’s surface can be measured in the form of image. The probe tip is coated with a thin film of ferromagnetic material that will react to the magnetic domains on the sample surface. The magnetic forces between the tip and the sample are measured by monitoring cantilever deflection while the probe is scanned at a constant height above the surface.
2.2.4 Transmission and Reflection Measurements

Transmittance and reflection measurements of the samples are used to determine the band gap of semiconductor. The band-gap of the sample is determined by observing the wavelength at which the sample begins to absorb the transmitted light. In order to measure the absorption accurately, we must account for the entire light incident, reflected, transmitted or scattered by the sample. The schematic of optical characterization set up is shown in the Fig. 2.12.

Fig. 2.12 Experimental set-up for transmission and reflection measurement of the thin film samples.

From the measurement of transmission and reflection of the thin films, the absorption coefficient ($\alpha$) was calculated using the Lambert’s law [38],

$$T = (1 - R)^2 \exp(-A) = (1 - R)^2 \exp(-\alpha t)$$  \hspace{1cm} (2.3)

where, $R$ is the reflectance, $T$ is the transmittance, $A$ is the absorbance, and $t$ is the film thickness. For an absorbing material, the absorption coefficient is given by [39],

$$\alpha = \frac{1}{d} \ln \left( \frac{T}{[1 - R]^2} \right)$$  \hspace{1cm} (2.4)

The absorption coefficient, $\alpha$, for a direct transition is related to the band gap of a semiconductor and is given by [40]:

$$ah\nu \propto \left( \nu - E_g \right)^{\frac{1}{2}}$$  \hspace{1cm} (2.5)
where $h\nu$ is the photon energy, and $E_g$ is the energy gap. Using the above equation, the plot of $(a\nu)^2$ versus $\nu$ gives the band gap of the material. For the band gap calculation of CIGS thin films we consider the reflection while for others i.e. CdS, i- and AZO only the transmission values are consider, as they are transparent.

### 2.2.5 Electrical Measurements

The van der Pauw technique of four-point probe measurement allows measurements of samples of arbitrary shape. Using four-point probe one can calculate the majority charge carrier density, $n_s$, and mobility, $\mu$, of a semi-conducting sample as a function of temperature. The van der Pauw technique, due to its convenience, is widely used in the semiconductor industry to determine the resistivity of uniform samples [41]. The inventor, van der Pauw, uses an arbitrarily shaped, thin-plate sample containing four very small point-ohmic contacts placed on the periphery, extreme ends of the plate.

**Resistivity Measurements**

The van der Pauw configuration having a rectangular shaped sample is shown in Fig. 2.13. The objective of the resistivity measurement is to determine the sheet resistance, $R_{sh}$. van der Pauw demonstrated that there are actually two characteristic resistances, $R_A$ and $R_B$, related to the sheet resistance $R_s$ through the van der Pauw equation,

$$ R_A = \frac{(R_{21,34} + R_{12,43} + R_{43,12} + R_{34,21})}{4}, \text{ and} $$

$$ R_B = \frac{(R_{32,41} + R_{23,14} + R_{14,23} + R_{41,32})}{4} \quad (2.6) $$

![Fig. 2.13 Schematic of a van der Pauw configuration used in the determination of the two characteristic resistances $R_A$ and $R_B$.](image-url)
Using $R_A$ and $R_B$, one can calculate the, $R_{sk}$ using the equation,

$$\exp(-\pi R_A/R_{sk}) + \exp(-\pi R_B/R_{sk}) = 1$$  \hspace{1cm} \text{(2.7)}$$

which can be solved numerically for $R_s$. The bulk electrical resistivity, $\rho$ can be calculated using,

$$\rho = R_{sk}d$$  \hspace{1cm} \text{(2.8)}$$

For the measurement of resistivity and sheet resistance of CIGS and CdS thin film, we follow the Van der Pauw method. While for molybdenum (Mo) and ZnO thin film we used the four-point probe method.

In four-point probe method (Fig. 2.14), the separate current and voltage electrodes are used for eliminate the contact resistance between the electrodes and the material. In particular, in the case of thin films, the distance between the two probe(s) is very high compared to the film thickness ($d$), and hence the sheet resistance ($\Omega/\square$) can be given as,

$$R_{sh} = k \frac{V}{I}$$  \hspace{1cm} \text{(2.9)}$$

where, $k$ is a constant dependent on the configuration and spacing of the contacts.

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**Fig. 2.14 Four-point probe arrangement for the measurement of sheet resistance of the thin film.**
If the film is large in extent compared with the probe assembly and the probe spacing is large compared with the film thickness, then \( k = \frac{\pi}{\ln 2} = 4.53 \). By using the Equations 2.8 and 2.9, we can find the resistivity of the thin film sample.

**Hall-effect**

A Hall-effect measurement, discovered by the Edwin Hall in 1879, is a valuable tool for material and device characterization [42]. Fundamentally, the Hall-effect can be observed when a combination of a magnetic field through a sample and a current along the length of the sample creates an electrical current perpendicular to both the magnetic field and the current. This creates a transverse voltage; perpendicular to both the magnetic field and the current (see Fig. 2.15). The fundamental principle is the Lorentz force, that is, the force on a point charge due to electromagnetic fields. The "right hand rule" allows determining the direction of the force on a charge carrier based on its direction of motion and the direction of the applied magnetic field.

![Hall-effect Diagram](image)

**Fig. 2.15 Illustration of Hall-effect, the hall voltage observed due to the Lorentz force.**

Measuring the Hall-effect of the thin film the following equipments are required:

- Permanent magnet, or an electromagnet (500 to 5000 Gauss)
- Constant-current source with currents ranging from 10 \( \mu \)A to 100 mA; Must satisfy the, \( I < (200R)^{0.5} \), condition
- High input impedance voltmeter ranging from 1 \( \mu \)V to 1 V
- Sample temperature-measuring probe (resolution of 0.1 °C for high accuracy work).

The Hall voltage measurement consists of a series of voltage measurements with a constant current, \( I \), and a constant magnetic field, \( B \), applied perpendicular to the plane of the sample.
Conveniently, the van der Pauw sample geometry, as shown in Fig. 2.16, used for the Hall measurement.

To measure the Hall voltage $V_{H}$, a current $I$ is forced through the opposing pair of contacts 1 and 3 and the Hall voltage $V_{H}$ ($= V_{24}$) is measured across the remaining pair of contacts 2 and 4. From the hall voltage, the sheet carrier density $n_s$ and hall mobility $\mu$ can be calculated. The procedure of the calculation is given below.

![Fig. 2.16 Schematic of a Van der Pauw configuration used in the determination of the Hall voltage $V_{H}$.](image)

**Hall Calculations**

Calculate the following (be careful to maintain the signs of measured voltages to correct for the offset voltage):

$$V_C = V_{24P} - V_{24N}, \quad \text{and} \quad V_D = V_{42P} - V_{42N}, \quad \text{and}$$

$$V_E = V_{13P} - V_{13N}, \quad \text{and} \quad V_F = V_{31P} - V_{31N}$$

(2.10)

The sample type is determined from the polarity of the voltage sum $V_C + V_D + V_E + V_F$. If this sum is positive (negative), the sample is p-type (n-type). The sheet carrier density (in units of cm$^{-2}$) is calculated from,

$$p_s = \frac{|8 \times 10^{-8} I_B|}{|q(V_C + V_D + V_E + V_F)|}$$

(2.11)

If the voltage sum is positive, if negative than;

$$n_s = \frac{|8 \times 10^{-8} I_B|}{|q(V_C + V_D + V_E + V_F)|}$$

(2.12)
where B is the magnetic field in gauss (G) and I is the dc current in amperes (A). From the values of sheet carrier density (n_s) and sheet resistance (R_{sh}) the mobility (\mu) of the sample is

$$\mu = \frac{1}{q n_s R_{sh}}$$  \hspace{1cm} (2.13)

where q = charge of the electron.

2.2.6 Current-Voltage (I-V) Measurements

We have developed the LabVIEW (Laboratory Virtual Instrument Engineering Workbench) controlled automation program for studying the solar cell I-V characteristics. The block diagram of experimental set-up used to measure solar cell I-V characteristics is shown in Fig. 2.17. The Metal Halide bulb (150 W) is used as an irradiation light source. Keithley 2420C source meter and 6½ digit Keithley 2000 multimeter are connected with computer using GPIB. The source meter and multimeter are configured in 4-wire configuration to eliminate the contact resistance value, which plays important role in terms of series resistance (R_s), and shunt resistance (R_{shu}) of the solar cell. The source meter capable to source and measure the voltage or current in the rage of 200 mV to 60 V and 10 \mu A to 3 A respectively. It can measure 1/00 readings/second at 4-1/2 digits via GPIB. The light intensities at various distances from the source were measured with the help of solarimeter (CEL, India).

![Fig. 2.17 The block diagram of the experimental set-up for the solar cell I-V characteristics measurement.](image)

The basic idea of the developed LabVIEW program for the solar cell I-V characteristics is to minimize the direct irradiation time of metal halide bulb to the solar cell. As the irradiation time is more the temperature of the solar cell increases so, the V_{oc} of the solar cell decreases because of the widening the depletion region. The useful parameters like solar cell efficiency (\eta), fill-factor (FF), open-circuit voltage (V_{oc}), short-circuit current (I_{sc}),
series resistance (R_s), and shunt resistance (R_sh) were directly evaluated from the I-V characteristic of the solar cell in very short time compared to the manual measurement.

The LabVIEW program, shown in Fig. 2.18, is used for measuring the I-V characteristics of the solar cell. The LabVIEW program has two parts, one is the dark I-V measurements and the other one is illuminated I-V measurements. By selecting the dark I-V tab form the front panel of the LabVIEW program. In the dark I-V set the parameters i.e. the start voltage, stop voltage, voltage source delay, voltage source steps. By selecting the data save option we can save the data (in .txt format) as well as curves (in .jpg format). Before run the program, the solar cell placed in the dark environment. When the program run, according to the value of source voltage range, steps and delay the source meter source the voltage and measure the current and plot the I-V of the solar cell. The ideality factor, n, and reverse saturation current, I_0 of the solar cell found from those curves.

![LabVIEW program for I-V measurements](image)

**Fig. 2.18** The front panel of the LabVIEW program for the I-V measurements in light as well as dark environment.

For the illuminated I-V, the solar cell is kept under the solar irradiation source. As mention above we have used metal halide (150 W) as a light source. After adjusting the input power to the solar cell, i.e. whether AM 1.5 or AM 1, set it in the program and then set the parameters i.e. start voltage, voltage source delay, voltage source steps and the temperature of
the solar cell. Select the data save option and run the program. The graph of illuminated I-V and P-V was plotted and from those plots the program find the solar cell parameters i.e. like \( \eta \), FF, \( V_{oc} \), \( I_{sc} \), \( R_s \), and \( R_{sh} \).

2.2.7 Spectral Response Measurements

Spectral response, i.e. Quantum efficiency (QE), measurements quantify the behavior of a device over a spectrum of light. In the generally, QE defined as ration of the optically generated electrons due to the monochromatic probe beam to the number of light photons incident.

\[
QE(\lambda) = \frac{\text{No.of electrons collected}}{\text{No.of incident photons}}
\]  

(2.14)

A tungsten halogen lamp is used as the light source at the input slit of the monochromator. The output beam of monochromator is chopped with the optical copper and focused into a 0.4 \( \times \) 0.4 cm area on the solar cell device. Using LabVIEW (Version 8.2) software, spectral response is measured in the range 350–1400 nm at 5 nm intervals at room temperature. Fig. 2.19 shows LabVIEW front panel for the measurement of spectral response.

![Fig. 2.19 The LabVIEW front panel for the measurement of spectral response of the solar cell.](image)

In the measurement process, the computer records the currents produced by the test device and the monitor photodiode one by one for each wavelength in the test. Using the
power to current ratio previously recorded, it converts the monitor current to a beam power quantity. The ratio of test device current \( I_{DUT}(\lambda) \) to beam power is the device responsivity.

\[
QE(\lambda) = \frac{h \cdot c \cdot I_{DUT}(\lambda)}{e \cdot \lambda \cdot I_{STD}(\lambda) \cdot R_{STD}(\lambda)} \times 100\%
\]  

(2.15)

Where \( h \) is Planck’s constant, \( c \) is the speed of light, \( e \) is the electron charge, \( I_{STD}(\lambda) \) is the standard detector current, and \( R_{STD}(\lambda) \) is the responsivity of the standard detector in W/A.