CHAPTER 2

Thin film deposition techniques and characterisation tools
Chapter 2

2.1 Introduction

Any solid or liquid object with one of its dimensions very much less than that of the other two may be called a ‘thin film’ [1]. Thin film devices would typically be about 5 to 50 \( \mu \text{m} \) thick in contrast to bulk devices, which are about 50 to 250 \( \mu \text{m} \) thick [2]. Again, it is not the thickness that is important in defining a film, but rather the way it is created with the consequential effects on its microstructure and properties. The microstructural features of the absorber layer sensitively influence the photovoltaic performance of a solar cell and in some cases, specific microstructures may be necessary to obtain the desired performance. A wide variety of microstructures and consequently properties can be obtained by simply varying the deposition conditions during the growth of the film. Thin film properties are strongly dependent on the methods of deposition, the substrate materials, the substrate temperature, the rate of deposition and the background pressure. The application and the properties of the given material determine the most suitable technique for the preparation of thin films of the material.

The different materials for the window layer, active layer and the transparent conducting electrodes for solar cells were prepared and characterised. Various deposition techniques were employed for the deposition of these materials in thin film form and the structural, optical and electrical properties of these films were studied using different characterisation tools. The various thin film deposition techniques and the characterisation methods employed are summarized in this chapter.

2.2 Thin film Preparation Techniques

Generally any thin film deposition follows the sequential steps: a source material is converted into the vapour form (atomic/molecular/ionic species) from the condensed phase (solid or liquid), which is transported to the substrate and then it is allowed to condense on the substrate surface to form the solid film [2]. Depending on how the atoms/molecules/ions/clusters of species are created for the condensation process, the deposition techniques
Thin film deposition techniques...

are broadly classified into two categories, viz. Physical methods and Chemical methods [2]. The general physical methods used in the work presented in this thesis are vacuum evaporation and sputtering. The vacuum evaporation techniques employed in the current work include, thermal evaporation by resistive heating, flash evaporation, and electron beam evaporation. All these physical methods of deposition of thin film were done in a high vacuum system in which a vacuum of $10^{-5}$ mbar was created using a diffusion pump backed by a rotary pump. RF magnetron sputtering was used for the preparation of transparent conducting oxide (tin doped indium oxide) thin films. Chemical bath deposition was effectively used to deposit certain II-VI chalcogenides (CdS and ZnS) semiconductors. Other special technique used in this work is the two stage processes, which involve the preparation of the precursor employing thermal evaporation followed by the sulphurisation. The following sections discuss the methodology and experimental set-ups used in various thin film depositions.

2.2.1 Thermal evaporation in vacuum by resistive heating

It is the most widely used technique for the preparation of thin films for the deposition of metals, alloys, and also many compounds, as it is very simple and convenient. Here the only requirement is to have a vacuum environment in which sufficient amount of heat is given to the evaporants to attain the vapour pressure necessary for the evaporation. The evaporated material is allowed to condense on a substrate kept at a suitable temperature.

When evaporation is made in vacuum, the evaporation temperature will be considerably lowered and the formation of the oxides and incorporation of impurities in the growing layer will be reduced. Evaporation is normally done at a pressure of $10^{-5}$ Torr. At this pressure a straight line path for most of the emitted vapour atoms is ensured for a substrate to source distance of nearly 10 to 50 cm [3]. The characteristics and quality of the deposited film will depend on the substrate temperature, rate of deposition, ambient pressure, etc. and the uniformity of the film depends on the geometry of the evaporation source and its distance from the source. The deposition by
thermal evaporation is simple, convenient and is widely used. Excellent and detailed reviews on the know-how of the thermal evaporation have been discussed by Holland [4].

Thermal evaporation has been used at various stages of the work. In the two-stage process for the preparation of CuInS₂ thin films, thermal evaporation was used to deposit In-Cu bilayers. Thin layer of vacuum evaporated indium or aluminium was used as electrodes in electrical measurements. Molybdenum boat was used as the evaporation source for the deposition of copper and indium, and tungsten coils were used for the deposition of aluminium.

2.2.2 Electron beam evaporation

In electron beam evaporation (EBE) a stream of electrons is accelerated through fields of typically 5–10kV and focussed onto the surface of the material for evaporation. The electrons lose their energy very rapidly upon striking the surfaces and the material melts at the surface and evaporates. That is, the surface is directly heated by impinging electrons, in contrast to conventional heating modes. Direct heating allows the evaporation of materials from water-cooled crucibles. Such water-cooled crucibles are necessary for evaporating reactive and in particular reactive refractory materials to avoid almost completely reactions with crucible walls. This allows the preparation of high purity films because crucible materials or their reaction products are practically excluded from evaporation [3,5].

Electron beam guns can be classified into thermionic and plasma electron categories. In the former type the electrons are generated thermionically from heated refractory metal filaments, rods or disks. In the latter type, the electron beams are extracted from plasma confined in a small space. We have used a thermionic system for the deposition of ZnS thin films. EBE was carried out in vacuum (2x10⁻⁵ mbar) using an electron beam gun of 6KW (make-Hind High Vacuum, Bangalore).
2.2.3 Flash evaporation

Flash evaporation is a technique for the deposition of films whose constituents have different vapour pressures. This method has the difficulty in controlling stoichiometry of the films due to the differences in the vapor pressure of the component elements [1,3]. In contrast to two-source evaporation, it does not require provisions to monitor the vapour density, nor is the control of the source temperature particularly critical. The objective of film-composition control is accomplished by evaporating to completion small quantities of the constituents in the desired ratio. Only one filament is used at a temperature sufficiently high to evaporate the less volatile material. The technique is applicable for the evaporation of alloys, metal-dielectric mixtures and compounds. In most cases, the vapours impinging on the substrate are highly supersaturated so that the film composition is not affected by condensation coefficients. Generally, the control of film composition is determined by how well the objective of complete evaporation of the source material is accomplished. For this purpose, several experimental techniques are available which are characterized by three criteria namely, the form in which the evaporant material is introduced, the mechanism used to dispense the evaporant and the type of flash filament employed. The greatest freedom in regard to the form of the evaporant material is when it is available in the powder form. Various powder dispensers are available, which have storage hoppers that differ in the powder release and transport mechanisms. The flash evaporation filament chosen depends on the nature of the evaporant material and it should be capable of attaining temperatures of typically 2000°C without volatilization or heavy reaction with the evaporant.

A universal problem encountered in the flash evaporation of powders from flat filaments is incomplete evaporation due to particle ejection and deflection. Since the evaporant has a large surface-to-volume ratio but can usually not be degassed prior to evaporation, the sudden release of gases upon impact on the filament is often sufficient to expel particles. Another loss mechanism is the deflection of falling powder away from the filament.
by the current of rising vapours. The latter effect is stronger at higher evaporation rates. Small particles are more strongly deflected than larger ones, which is the reason for using graded powders. In the evaporation of homogenous powders such as compounds or alloys, particle ejection and deflection affect only the economy of the process and the maintenance of the vacuum system. There is also a risk that particles may be thrown against the substrate surface. To avoid these difficulties, coarser powders and cylindrical or conical crucibles have been used in the evaporation of pervoskites and III-V compounds.

Flash evaporation has mostly been performed in poor vacuum of $10^{-5}$ to $10^{-4}$ Torr. This is attributable to the high gas content of the evaporant powder and outgassing from the surfaces surrounding the relatively large-area flash filament. The effect of the high background pressure on film properties may be inconsequential, especially in the case of oxide films. However, this is not so if strongly electropositive metals are deposited. The temperature of the substrates determines primarily the degree of order and crystallinity of the films.

Flash evaporation technique has been used for the deposition of the copper indium selenide thin films. The copper indium selenide powder with the desired composition ratio was prepared by the solid-state reaction of the constituent elements. The flash evaporation was carried out in a vacuum chamber at a base pressure of $2 \times 10^{-5}$ mbar. The powder was taken in a specially designed stainless steel crucible, which was connected to a vibrator. The speed of the vibrator was controlled externally. The CuInSe$_2$ powder coming out of the groove of the crucible was channelled to fall on to the hot molybdenum boat using a glass chute. The outgassing occurred during the flash evaporation resulted in the variation of vacuum in the range $2 \times 10^{-5} - 5 \times 10^{-3}$ mbar. The films were deposited on cleaned glass substrates, which were kept at 10 cm above the evaporation source. The deposition was carried out without any intentional heating of the substrate. The evaporation itself has raised the temperature of the substrate to around 100°C. The thickness of the films during deposition was monitored using a digital
thickness monitor. The as deposited CuInSe₂ thin films were found to be selenium deficient and hence they were subjected to selenisation to compensate the loss of selenium in the film.

2.2.4 Sputtering

Sputtering is one of the most versatile techniques used for the deposition of transparent conductors when device quality films are required. Sputtering process produces films with higher purity and better controlled composition, provides films with greater adhesion and homogeneity and permits better control of film thickness. The sputtering process involves the creation of gas plasma usually an inert gas such as argon [6] by applying voltage between a cathode and anode. The cathode is used as a target holder and the anode is used as a substrate holder. Source material is subjected to intense bombardment by ions. By momentum transfer, particles are ejected from the surface of the cathode and they diffuse away from it, depositing a thin film onto a substrate. Sputtering is normally performed at a pressure of 10⁻² – 10⁻³ Torr.

Normally there are two modes of powering the sputtering system; dc and rf biasing. In dc sputtering system a direct voltage is applied between the cathode and the anode. This method is restricted for conducting targets only. RF sputtering is suitable for both conducting and non-conducting targets; a high frequency generator (13.56 MHz) is connected between the electrodes of the system. Magnetron sputtering is a process in which the sputtering source uses, magnetic field at the sputtering target surface. Magnetron sputtering is particularly useful when high deposition rates and low substrate temperatures are required [7].

Both reactive and non-reactive forms of dc, rf and magnetron sputtering have been employed for the deposition of compound semiconductors. In reactive sputtering, the reactive gas is introduced into the sputtering chamber along with argon to deposit oxide films. The deposition rates and properties of the films strongly depend on the sputtering conditions such as the partial
pressure of the reactive gas, the sputtering pressure, substrate temperature and spacing.

The process of RF sputter deposition is made possible due to the large difference in mass, and hence mobility, of electrons and inert gas ions. Because electrons are many times less massive than ions, electrons attain much greater velocities and travel much further than ions during each cycle of the applied rf voltage waveform. Since electrons travel much further, they eventually accumulate on the target, substrate and chamber walls such that the plasma is the most positive potential in the system. These induced negative voltages or “sheath voltages”, cause acceleration of positive ions toward the negatively charged surfaces, which subsequently leads to sputtering events. The volume adjacent to a surface tends to be relatively free of electrons because of the negatively charged surface. This leads to a “dark space” because electrons are not available to excite gas atoms [8]. A schematic diagram of the rf sputtering system is shown in figure 2.1.
The target is selectively sputtered by controlling the relative surface areas of the target and the substrate holder. If space charge limited current is assumed, the ion current flux, \( J \) can be estimated by the Child- Langmuir equation [8],

\[
J = \frac{KV^{3/2}}{D^2m_{\text{ion}}}
\]  

(2.1)

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

\[
\frac{A_A V_A}{D_A^2} = \frac{A_B V_B}{D_B^2}
\]  

(2.2)

Where \( A_A \) and \( A_B \) are the surface areas of electrodes A and B respectively. It should be noted that this step differs from the assumption of treating the positive ion current densities equal. If the positive ion current densities were equal, there would be a much greater positive ion current flowing during one half cycle of the applied voltage waveform than the other due to the much greater area of the grounded substrate electrode. Therefore, because this system is assumed to be in steady state, the total positive ion current per half cycle should be the relevant quantity.

The glow discharge itself is a region where large quantities of positive and negative charge exist and can be modelled as a wire. Since most of the voltage in the glow discharge is dropped across the dark space, and they have small conductivities, they can be modelled as capacitors such that the capacitances,

\[
C \propto \frac{A}{D}
\]  

(2.3)

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

\[
\frac{V_A}{V_B} = \frac{C_B}{C_A}
\]  

(2.4)

From equations (2.1), (2.2) and (2.3),

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

(2.5)
Chapter 2

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

We have used an in-house made magnetron for the rf sputtering of tin doped Indium oxide thin films. A magnet of 2000gauss was used to deflect the ions. A schematic diagram of the magnetron is shown in figure 2.2. The vacuum system consists of a six-inch diameter diffusion pump backed by a rotary pump (make – Indovision, Bangalore). The rf supply was connected to the magnetron through a capacitive matching network (make–Digilog

![Schematic structure of the magnetron](image)

**Fig 2.2** Schematic structure of the magnetron
Thin film deposition techniques...

Instruments, Bangalore). The flow of argon gas into the vacuum chamber was controlled using a mass flow controller (make Bronkhorst, Holland).

2.2.5 Chemical bath deposition

Unlike the physical methods of preparation of thin films involving evaporation or ejection of material from a source, chemical methods of thin film deposition entail a definite chemical reaction. Chemical methods for film deposition in general use simpler equipment and are more economical than physical approaches. Moreover, chemical methods do not require high vacuum and can be carried out at lower temperatures. CBD is a simple and low cost method that produces uniform, adherent and reproducible large area thin films for PV related applications [9].

In chemical bath deposition, a complexing agent is used to bind the metallic ions to avoid the homogeneous precipitation of the corresponding compound. Formation of complex ion is essential to control the rate of the reaction and to avoid the immediate precipitation of the compound in the solution. The metal complex hydrolyses slowly to generate the positive ions in the solution. The solution containing the metal complexes was mixed with the solution which produces the negative ion by hydrolyses. The deposition of the compound occurs when the ionic product exceeds the solubility product of the compound to be deposited. Either homogeneous or heterogeneous deposition can occur. The homogeneous process is the faster one resulting in the adsorption of powdery particles on the substrate due to the bulk precipitation. So, the formation of metal complexes is essential to minimize the homogeneous process. In the heterogeneous process, due to the slow release of the ions by the metal complexes, the preferential adsorption of the ions will take place leading to the uniform nucleation and growth of the thin film.
Chapter 2

The main disadvantage of the chemical bath deposition is the wastage of the material due to the deposition on the walls of the container and precipitation into the solution. Preparation of the films with a definite geometric pattern on the substrate is difficult because perfect masking is not possible. The quality of the film deposited depends on the bath parameters like temperature, time of deposition, concentration of the reactants and the pH of the chemical bath. The experimental set up for the chemical bath deposition is shown in figure 2.3.

Although chemical bath deposition has been used as a technique for preparing films since 1960, utilization of CBD semiconductors in photovoltaic devices started only by 1990 by integrating CdS buffer layer over sputtered ZnO films [10]. A number of review articles discussing the status and applications of CBD have been appeared in the literature [9,11,12]. In this thesis work CdS, ZnS and their ternary derivative Zn$_x$Cd$_{1-x}$S thin films were deposited by the chemical bath deposition technique. Detail reaction mechanism during the chemical bath deposition and the role of the complexing agents are discussed in chapter 3.
2.2.6 Two stage process

Two stage processes is a simple method for the preparation of chalcogenide and selenide thin film [13]. This method has been effectively employed to produce high efficiency solar cells. The two stage processes consists of two steps; 1) Preparation of the precursor 2) chalcogenisation of the precursor. The precursor can be, evaporated or sputtered metallic layers or a metallic alloy formed by the annealing of metallic multilayers. We have used the two stage processes to prepare copper indium sulphide (CuInS$_2$) thin films. Here Copper and Indium layers are deposited on glass substrates by thermal evaporation. The Cu-In bi-layer is annealed in vacuum to form the copper indium alloy (Cu$_{11}$In$_{9}$). This alloy was sulphurised at various temperatures to form CuInS$_2$ thin films. Sulphurisation was carried out in a specially designed set up as shown in figure 2.4. The set up consists of a reaction vessel made of quarts, temperature controlled heater and the sulphurisation source. H$_2$S was used as the sulphurising agent, which was prepared using a Kipp’s apparatus by the reaction between dilute hydrochloric acid and ferrous sulphide. The sulphurisation temperature was varied from 250$^0$C to 400$^0$C.

![Fig 2.4 Sulphurisation set up for the preparation of CuInS$_2$](image)
2.2.7 Selenisation set up

The flash evaporated CuInSe₂ thin films were found to be selenium deficient [13] and hence post deposition annealing in selenium was carried out to compensate the selenium loss. The set up used for the selenisation is as shown in figure 2.5.

![Selenisation set up](image)

Fig. 2.5 Selenisation set up

Two heating zones are used for the selenisation as shown in the figure 2.5. The selenium pellets at the heating zone 1 will be sublimated and the selenium vapours will be carried to the heating zone 2 by the nitrogen gas. The selenium vapour will react with the CuInSe₂ films, which is kept at a temperature of 400°C resulting in a chalcopyrite CIS film.

2.3 Characterisation tools

The optimisation of the preparation conditions is the main task in order to get device quality films. This is to be done on the basis of detailed structural, compositional, morphological, optical and electrical properties of the films obtained at different growth conditions. In the following sections the techniques used for the film characterizations are discussed briefly.

2.3.1 Thin film thickness

Thickness plays an important role in the film properties unlike a bulk material. Reproducible properties are achieved only when the film thickness
and the deposition parameters are kept constant. Film thickness may be measured either by in-situ monitoring of the rate of deposition or after the film deposition.

**Gravimetric method**

The method depends on the increase of the weight \( w \) of a film due to its mass increase and from the knowledge of its density \( \rho \) and the deposit area \( A \) [2]. The film thickness ‘\( t \)’ can be evaluated from the relation,

\[
t = \frac{w}{\rho A}
\]  

(2.6)

The increase in weight ‘\( w \)’ was measured using a microgram balance. This method was used for calculating the thickness of the chemical bath deposited ZnS films and the CuInS\(_2\) films prepared by the two-stage process.

**Quartz crystal monitor**

This method was first investigated by Sauerbrey [14] independently and later modified by Lostis [15] and many others. In this in-situ method, thickness measurement depends on the oscillation of a quartz crystal when excited and the frequency of its oscillation depends on its thickness as given by the relation [2],

\[
f = \frac{v}{2d} = \frac{N}{t} (\text{nmkc} / \text{sec}) \]

(2.7)

where, \( v \) is the velocity of the transverse elastic waves normal to the crystal plate, \( d \) is the thickness of the crystal and \( N \) is the frequency constant depending on the nature of the crystal.

When a film of thickness \( t \) is deposited on the quartz plate, the mass of the crystal changes. The corresponding change in the frequency of the crystal can be utilised to find the average thickness of the film deposited.

\[
t = \frac{\Delta f}{C \sigma}
\]  

(2.8)

where, \( \sigma \) is the density of the deposited film and \( C = \frac{f^2}{N \rho} \) (\( \rho \) is the density of the quartz crystal) is called the sensitivity for mass determination which is a constant of the crystal used. We have used a quartz thickness monitor
Chapter 2

(Model C200) in which the changes in the resonant frequency of the quartz crystal oscillator with the film deposition is calibrated to give the deposition rate and the thickness of the film. The quartz thickness monitor was used during the flash evaporation of CuInSe₂ films, electron beam evaporation of ZnS and in the deposition of In and Cu layers in the two stage processes.

**Optical interference method**

Film thickness can be measured accurately from interference fringes using multiple beam interferometry. This technique was first used by Weiner [16] and later was modified by Tolansky [17]. Two reflecting surfaces are brought in close proximity such that a small wedge with a small air gap in between them is formed. If a monochromatic light falls at normal incidence on it, interference of light due to the multiple reflected beams results in a series of fringes (Fizeau). The distance between the fringes depends on the air gap as well as on the wavelength of the monochromatic light.

The film for thickness measurement is deposited on a flat surface so as to leave a sharp edge between the film and the uncoated region of the substrate. Over this film a highly reflecting coating of aluminium forms a sharp step on the film edge. Another optically flat glass slide known as the reference plate with a partially transparent aluminium film is then placed over the specimen with the metal coated surfaces in contact with each other so as to leave a small air gap at the step. A monochromatic parallel beam of light is then incident on this two plates assembly and reflected light is then observed through a microscope. A set of sharp fringes perpendicular to the step with equal displacements will be observed and the thickness \( t \) can be determined using the relation,

\[
t = \frac{b\lambda}{2a}
\]

(2.9)

where \( b \) is the displacement of the fringes at the step and \( a \) is the distance between consecutive fringes. The sharpness of the fringes depends on the reflectivity of the metal coating, the spread of the incident beam, air gap etc. This method was used for determining the film thickness of rf magnetron sputtered ITO films and chemical bath deposited CdS and ZnₓCd₁₋ₓS films.

42
2.3.2 Surface morphology

The uniformity and roughness of the thin film surface plays an important role in the optical properties of thin films. When the surface is rough, the films will be less transparent and the grain boundaries will affect the electrical properties of the thin films. The surface morphology of the films is studied using scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Scanning electron microscopy (SEM) is one of the most widely used techniques for obtaining micro structural and surface features of thin films. An electron beam is focused onto the surface of the specimen and results in the ionization of the atoms in the specimen. This will cause the ejection of the secondary electrons from the surface, very close to the incident beam position. These secondary electrons can be attracted to a positively charged detector with high efficiency. The secondary electron yield per primary electron is high and increases as the angle between electron beam and the surface normal increases [18]. The secondary electrons generated from the specimens are used for Z-modulation in a corresponding raster on an oscilloscope. In order to avoid charging problems a thin layer of gold is deposited on the specimen without altering the surface features. The secondary electron mode is generally preferred for topographical feature determination since these electrons generate only from about 10Å or less from the film surface and hence the picture obtained is a faithful reproduction of the surface features.

The scanning electron microscopy can be effectively used for the surface analysis to know the details regarding the grain size, presence of minor or secondary phases, the orientation of the grains, uniformity, porosity of the sample etc. SEM gives a pictorial overview of the grains on the thin film surface, whereas AFM is an effective tool to study the surface roughness and also the average cluster size on the thin film surface. AFMs can achieve a
resolution of 10 pm, and unlike electron microscopes, can image samples in air and under liquids.

2.3.3 Energy dispersive X-ray analysis (EDX)

EDX was used to estimate the composition of the thin film samples. X rays are generated by the incident electrons within a volume similar to but rather larger than that for the backscattered electrons. Peak X-ray energies corresponding to the characteristics of the elements within that volume can be identified and the relative compositions of elements can be estimated. Thus the bulk composition of the sample and of the individual grains in a polycrystalline sample can be determined [18].

2.3.4 X-ray diffraction studies

Electrical and optical properties of the materials are influenced by the crystallographic nature of the films. X-ray diffraction (XRD) studies were carried out to study the crystallographic properties of the thin films prepared.

A given substance always produces a characteristic X-ray diffraction pattern whether that substance is present in the pure state or as one constituent of a mixture of substances. This fact is the basis for the diffraction method of chemical analysis. The particular advantage of X-ray diffraction analysis is that it discloses the presence of a substance and not in terms of its constituent chemical elements. Diffraction analysis is useful whenever it is necessary to know the state of chemical combination of the elements involved or the particular phase in which they are present. Compared with ordinary chemical analysis the diffraction method has the advantage that it is much faster, requires only very small sample and is non destructive [19].

The basic law involved in the diffraction method of structural analysis is the Bragg’s law. When monochromatic X-rays impinge upon the atoms in a crystal lattice, each atom acts as a source of scattering. The crystal lattice
Thin film deposition techniques...

acts as series of parallel reflecting planes. The intensity of the reflected beam at certain angles will be maximum when the path difference between two reflected waves from two different planes is an integral multiple of $\lambda$.

This condition is called Bragg’s law and is given by the relation,

$$2d\sin \theta = n\lambda$$  \hspace{1cm} (2.10)

where $n$ is the order of diffraction, $\lambda$ is the wavelength of the X-rays, $d$ is the spacing between consecutive parallel planes and $\theta$ is the glancing angle (or the complement of the angle of incidence)[20].

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

The average grain size of the film can be calculated using the Scherrer’s formula [19],

$$d = \frac{0.9\lambda}{\beta \cos \theta}$$  \hspace{1cm} (2.11)

where, $\lambda$ is the wavelength of the X-ray and $\beta$ is the full width at half maximum intensity in radians.

The lattice parameter values for different crystallographic systems can be calculated from the following equations using the (hkl) parameters and the interplanar spacing $d$.

Cubic system,

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$  \hspace{1cm} (2.12)

Tetragonal system,

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$  \hspace{1cm} (2.13)

Hexagonal system,

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$$  \hspace{1cm} (2.14)

X-ray diffraction measurements of the different films were done using Rigaku automated X-ray diffractometer. The filtered copper K\(\alpha\) ($\lambda = 1.5418\text{Å}$) radiation was used for recording the diffraction pattern.
Chapter 2

2.3.5 Optical characterisation

**Determination of band gap energy**

Intrinsic optical absorption of a single photon across the band gap is the dominant optical absorption process in a solar cell. When the energy of the incident photon ($h\nu$) is larger than the band gap energy, the excitation of electrons from the valence band to the empty states of the conduction band occurs. The light passing through the material is then absorbed and the number of electron hole pairs generated depends on the number of incident photons $S_0(\nu)$ (per unit area, unit time and unit energy). The frequency $\nu$ is related to the wavelength $\lambda$ by the relation, $\lambda = c/\nu$, where $c$ is the velocity of light. The photon flux $S(x, \nu)$ decreases exponentially inside the crystal according to the relation [13],

$$S(x, \nu) = S_0(\nu) \exp(-\alpha x)$$  \hspace{1cm} (2.15)

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

According to Bardeen et al. [21] for the parabolic band structure, the relation between the absorption coefficient ($\alpha$) and the band gap of the material is given by,

$$\alpha = \frac{A}{h\nu} (h\nu - E_g)^r$$  \hspace{1cm} (2.16)

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

$$I = I_0 e^{-\alpha t}$$  \hspace{1cm} (2.17)

where, $I$ is the transmitted intensity and $I_0$ is the incident intensity of the light and $t$ is the thickness of the film. In the case of direct transition, from equation.2.16, $(\alpha h\nu)^2$ will show a linear dependence on the photon energy ($h\nu$). A plot of $(\alpha h\nu)^2$ against $h\nu$ will be a straight line and the intercept on energy axis at $(\alpha h\nu)^2$ equal to zero will give the band gap energy.
**Determination of optical constants**

The optical constants, the refractive index \((n)\) and the extinction coefficient \((k)\) of the films are calculated using the theory of Manificer et al. [22] for weakly absorbing films.

In the case of weakly absorbing films, the measurement of transmission of light through the film in the region of transparency gives the complex refractive index, \(n^* = n - ik\).

In the case of normal incidence and weak absorption, \(k^2 \ll (n - n_0)^2\) and \(k^2 \ll (n - n_1)^2\). If \(n_0\), \(n\) and \(n_1\) are the refractive indices of the substrate, film and the medium respectively, then the refractive index of the film is given by,

\[
 n = \left[ N + \left( N^2 - n_0^2 n_1^2 \right)^{1/2} \right]^{1/2}
\]

where,

\[
 N = n_0^2 + n_1^2 + 2n_0 n_1 \frac{T_{\text{max}} - T_{\text{min}}}{T_{\text{max}} T_{\text{min}}}
\]

where, \(T_{\text{max}}\) and \(T_{\text{min}}\) are found out from the interference fringes of the transmission spectra by fitting envelops for the maximum and minimum values.

The extinction coefficient \((k)\) can be calculated using the relation,

\[
 \alpha = \frac{4\pi k}{\lambda}
\]

where, \(\alpha\) is the absorption coefficient for the wavelength \(\lambda\) which can be found out from the transmission spectra.

**2.3.6 Electrical characterisation**

**Resistivity by two probe method**

The resistivity of the films is determined by the two-probe method with the electrodes in planar geometry. Evaporated indium layers or high conducting silver paste was used as the electrodes. The current voltage measurements were carried out using a Keithley’s source measure unit (Model SMU236). The resistivity \((\rho)\) of the films is calculated applying ohm’s law, by the relation \(\rho = RA/L\). Where R is the resistance given by the slope of the
current- voltage characteristic curves. A is the area of the film in planar geometry which is given by the product of the film thickness and the width of the film. L is the spacing between the electrodes.

**Hall measurement**

The electrical resistivity of a semiconductor thin film can be written using Ohm’s law,

\[ \rho = \frac{1}{en\mu} \]  

(2.21)

where ‘\( \rho \)’ is the film resistivity, e is the electronic charge, n is the number of carriers corresponding to the carrier concentration and ‘\( \mu \)’ is the carrier mobility. According to Ohm’s law the carrier mobility affects resistivity. Low resistivity can be achieved by increasing the carrier concentration or mobility or both. Increasing carrier concentration is self-limiting because at some point the increased number of free carriers decreases the mobility of the film due to carrier scattering. Hence there is a trade off between the carrier density and carrier mobility for achieving low resistivity.

In the case of Indium tin oxide films, the resistivity (\( \rho \)), carrier concentration (n), carrier mobility (\( \mu \)), and sheet resistance were measured using Vander Pauw four point probe in geometry [23]. Samples used were 1cm x 1cm in size. The ohmic contacts were made using silver paste. The silver paste was applied at the corners of the sample symmetrically as shown.

Let \( R_1 \) be the potential difference between A and B per unit current through C and D or vice versa. Similarly \( R_2 \) the potential difference between B and C per unit current through D and A.

Then sheet resistance \( R_s \) can be calculated using the relation
Thin film deposition techniques…

\[ R_s = \left( \frac{\pi}{\ln 2} \right) \left( \frac{R_1 + R_2}{2} \right) f \left( \frac{R_1}{R_2} \right) \]  
(2.22)

where \( f \left( \frac{R_1}{R_2} \right) \) is the Vander Pauw function and is given by the relation,

\[ f \left( \frac{R_1}{R_2} \right) = 1 - 0.3466 \frac{R_1 - R_2}{R_1 + R_2} \]  
(2.23)

The Hall signal was measured between two ends while passing the current through the other two ends. Hall mobility is,

\[ \mu = \Delta R \times \frac{10^8}{BR_s} \]  
(2.24)

where \( \Delta R \) is the change in resistance due to magnetic field (B) which was applied to measure Hall voltage. Carrier concentration was determined using the equation 2.21. The hall coefficient \( R_h \) is given by,

\[ R_h = \mu x \rho \]  
(2.25)

The type of carriers can be understood from the sign of the \( R_h \). The negative values of \( R_h \) correspond to the electrons (n-type) carriers and positive values to holes (p-type).

**Nature of conductivity**

Thermo power measurement is a useful technique for the evaluation of the type of carriers responsible for the conduction. Thermo power measurements were carried out using a modified set up [24] which is similar to the one designed by D.L. Young et al.[25]. The slope of the thermoemf versus \( \Delta T \) curve gives the Seebeck coefficient. A positive Seebeck coefficient is obtained when the majority carriers are holes and a negative Seebeck coefficient for electrons.
Chapter 2

References

Thin film deposition techniques ...