The chapter describes the experimental techniques used in the present investigation. A spectrum of characterization tools have been utilized to study the structural, morphological, compositional, chemical, optical, electrical and photovoltaic properties of films, powder, nanoparticles and solar cells. Principles of each technique are briefly discussed and specific conditions maintained during their application are stated.
3.1 Introduction

The present study is concerned with preparation/synthesis of CTS films and application in solar cells. Hence, the work involved different experimental techniques as shown in Fig. 3.1. This chapter describes briefly the instruments and set-ups used for carrying out the study.

![Diagram showing the techniques and instruments used in the present study.](image)

**Fig. 3.1:** The techniques and instruments used in the present study

3.2 Deposition of films

3.2.1 Dip-coating

Dip coating is a deposition technique where the substrates is immersed into the liquid and slurry, resulting in a coating of liquid onto the substrate. The coating may or may not be required to be processed to yield the final film. Dip coating can be done batch wise or continuously in case of sheets. The batch dip coating can be divided into five stages, schematically shown in Fig. 3.2 These five stages are: (i) immersion, (ii) start-up, (iii) deposition, (iv) drainage, (v) evaporation. The steps of deposition and drainage occur simultaneously. The evaporation may also occur concomitant to the process. The most critical point in the entire deposition is the boundary of substrate which is in direct contact with fluid and is called as dynamic wetting line.


Fig. 3.2: Five stages of batch dip-coating: (a) immersion, (b) start-up, (c) deposition and drainage, (d) drainage, (e) evaporation. (adapted from Ref. [1])

In dip coating the deposition occurs on both sides of substrates. The thickness of the film is governed by the two intersecting flows along the substrate, while drawing the substrate from the bath. One flow moving upward with substrate and other falling back into the bath. In the middle of these lies a layer which is stagnant and that’s what exactly controls the thickness. The location of this stagnant layer can be manipulated by viscosity, surface tension, density of the liquid and speed of drawing.

The thickness $h(x)$ is a direct function of the streamline. In an excellent review, Scriven [1] has described that there are as many as six different forces involved when the substrate is drawn from the bath. When the viscosity of liquid and drawing speed is higher enough to lower the curvature of meniscus, the thickness of the films is the location which balances the viscous drag and gravity force:

$$h = C_1 (\eta U_o / \rho g) \quad \ldots \quad (3.1)$$

where, $C_1$ is a constant with a value of 0.8 for Newtonian fluids.

When the viscosity ($\eta$) of liquid and surface tension ($\gamma$) both are low the balance is controlled by ratio of viscous drag to liquid-vapour surface tension and the relation is due to Landau and Levich:

$$h = 0.94 \left( \frac{\eta U_o}{\gamma_{LV}} \right)^{2/3} \left( \frac{\rho g}{\gamma_{LV}} \right)^{1/6} \quad \ldots \quad (3.2)$$

In general, slower the rate of lifting, smaller is the viscous drag and thinner will be the film deposited. When the thickness goes below a micron, a force known as disjoining force (arising from London intermolecular forces) becomes active. However, there is a limit to film thickness, implying that the thickness cannot be reduced further by lowering lifting rate. This is the case when disjoining pressure depends upon film thickness and the liquid wets the substrate homogenously.
At the same time, even at higher lifting rate, there can be number of factors restricting the thickness of film for eg. evaporation. Evaporation becomes considerable if the environment above the bath is not saturated with the volatile component. In case of higher evaporation rate the thickness of films may reduce drastically, the volatile component evaporate completely leaving behind the non-volatile component in crystalline or non-crystalline form with compact or porous structure. The microstructure of film is governed by: (i) precursor structure and reactivity, (ii) capillary force and (iii) withdrawal rate.

For thinner films, the vapour pressure is dependent on disjoining force, thus evaporation rate becomes dependent on the film thickness as the chemical potential tends to depend upon the thickness. Since the heat is readily available from surface underneath the coating, evaporation is inefficient to lower the temperature. The evaporation in this case is rather governed by movement of volatile liquid within the neighbourhood of substrate (few millimeter away from the substrate). This is described by convective diffusion and empirically expressed by the mass transfer coefficient ‘k’. The rate of evaporation is thus related quantitatively on the difference of partial pressure of volatile at the substrate and its neighbourhood.

Formation of inorganic film occurs as inorganic precursor concentrates upon the substrate due to gravitational draining and evaporation. Because of the increasing concentration of precursor in the proximity, non-volatile precursor species start aggregating, whereas, the repulsive forces start structuring the species as per the withdrawal rate. In case of reactive species, a competition may exist between the compaction due to evaporation or due to various condensation reactions. A combined effect is the collapsing of structure by capillary pressure created by liquid vapour menisci as it recedes into film interior [2].

The thickness of the film changes continuously due to the dynamic draining and evaporation. However, at the dynamic wetting line, the product of thickness, h and volume fraction of solid must remain constant. Thus volume fraction of solid varies inversely with thickness of film. In general, for planar substrate there exist a parabolic profile and it should vary as \( x^{1/2} \) (Fig. 3.3).
3.3 Structural characterization

3.3.1 X-ray Diffraction [3]

Solids can be broadly classified in two categories: (i) Amorphous and (ii) Crystalline. In amorphous solids, the constituent units (atoms or molecules) are localized randomly in space. Ordering, if exists, extends only to few neighbors. Glasses are example of amorphous solids.

In crystalline solids, however, the constituent units (atoms, molecules, ions, clusters) are orderly arranged. In Cartesian space, any crystalline substance can be visualized to be a repetition of minimal cuboidal volume, known as unit cell. Surprisingly, the there can be only 14 different unit cells in 3-dimensions, known as Bravais lattices. These patterns differ in six different dimensional parameters, which are lengths of three dimensions along the orthogonal axes (a along x, b along y, c along z) and angles between these three dimensions (α, β, γ) of the cuboid.

When electromagnetic radiation is incident on matter, electrons in the atoms tend to oscillate with same frequency as that of electric field of electromagnetic radiation, leading to elastic scattering of X-ray photon in different directions. These scattered photons from different atoms interfere with each other. In almost all directions
destructive interference will occur, that is, the combining waves are out of phase and there is no resultant energy leaving the solid sample. However the atoms in a crystal are arranged in a regular pattern, and in a very few directions constructive interference will occur. Hence, a diffracted beam may be described as a beam composed of a large number of scattered rays mutually reinforcing one another. The condition for constructive interference is given by Bragg’s law:

\[ n \lambda = 2d \sin \theta \quad \ldots \ldots \quad (3.3) \]

where \( n \) is an integer, \( \lambda \) is the wavelength of incident wave, \( d \) is the spacing between the planes in the atomic lattice, and \( \theta \) is the angle between the incident ray and the scattering planes.

Crystalline solids can be broadly categorized as single crystal and polycrystalline composed of grains (volume of orderliness) separated by disordered regions (grain boundaries). Depending on the extent of crystallinity (range of orderliness) or size of grains, polycrystalline solids can be classified as (with typical grains size in parentheses): (i) multicrystalline (>1 mm), (ii) microcrystalline (1000 \( \mu \)m to 100 nm) and nanocrystalline (> 100 nm). Since in a polycrystalline materials the grains or crystallite are randomly oriented, the X-ray diffractometers used to study them are different than that for single crystals, are called powder X-ray diffractometers. The powder X-ray diffractometer works on assumption that the crystallites in the powder sample are completely randomly oriented. This orientational averaging causes the three-dimensional reciprocal space that is studied in single crystal diffraction to be projected onto a single dimension. Cause of this the geometrical design of a single crystal X-ray diffractometer and powder X-ray diffractometer differs a lot. Schematic of design of a typical geometry known as coupled Theta-2Theta (Bragg-Brentano) used for powder diffraction is shown in Fig. 3.4.
**Fig. 3.4:** Schematic of coupled theta-2theta (Bragg-Brentano) geometrical design used in Powder X-ray diffractometer.

Powder X-ray diffraction has its own advantages and disadvantages over single crystal X-ray diffraction, since it is not always possible to have single crystal samples. Since the samples synthesized in this study are polycrystalline, a powder X-ray diffractometer has been employed. Hereafter, the powder X-ray diffraction or diffractometer will be termed as X-ray diffraction or diffractometer only.

X-ray diffraction provides both qualitative i.e. phase identification as well as quantitative (such as lattice parameters and mix phase composition) information. The peak position consists of information such as symmetry, unit cell dimensions and qualitative phase identification, while peak intensities indicate the content of unit cell and quantitative phase fraction. For a polycrystalline solids specially, the shape and broadening (full width at half maximum), if any, gives crystallite size and strain. The peak broadening in diffraction patterns can arise due to instrumental effects, finite crystallite (>100 nm), strain (deviation from ideal positions) and extended defects. As the peak broadening can arise from number of factors, it must be corrected first for instrumental broadening and broadening due to strain. After these corrections the crystallite size can be extracted from peak broadening. Scherrer relation is one such method to obtain average crystallite size, the relation is as:

\[
D = \frac{(0.9\lambda)}{(\beta \cos \theta)} \tag{3.4}
\]
where, D is average crystallite size, $\lambda$ is the incident X-ray wavelength, $\beta$ is full width at half maximum (FWHM) and $\theta$ is the peak position.

X-ray Diffractometer used in this study is Bruker D2 phaser with Ni filtered Cu K\textsubscript{\textalpha} radiation source of 1.5418 Å wavelength (Fig. 3.5). The powder samples are first ground and then filled in a disk like sample holder and films were mounted as such. Unless, specified all the data is collected with step size 0.02° in shown 2theta range.

![Fig 3.5: Powder X-ray Diffractometer (Bruker, D2 Phaser) used in present study](image)

3.3.1a Rietveld Refinement

For quantitative structure determination, full profile Rietveld refinement is done using Topas 4.2 software. In this study, mostly the refinement is performed upon sphalarite (otherwise stated) as the starting structure. Peak fitting have been carried out using SPV-II function which is composite of Gaussian and Lorentzian functions. The background is refined using sixth order Chebyshev polynomials. Thermal parameters are constrained to fixed range and sum of occupancies at mixed site have been set to 1.

3.3.2 Raman spectroscopy [4]

Raman spectroscopy is a kind of spectroscopic tool which relies on the phenomenon of inelastic scattering of monochromatic light. In general, when a beam of monochromatic photons interacts with matter photons are absorbed and reemitted from system. The reemitted photons from the system may have the same wavelength as the incident photon called as elastic scattering (Rayleigh scattering) or may have different
wavelength than the incident photon called as inelastic scattering and this also known as the Raman effect. The difference or the shift in the wavelength of the incident photon arises due to the interaction of the incident photon with various vibrational or rotational modes and phonons. Thus provides useful information about structural features of the system, which can be solid, liquid or gas.

3.3.2.1 Origins of Raman scattering

When electromagnetic wave with electric field vector $\mathbf{E}$ interacts with the molecule, it deforms the molecule as per its polarizability, $\alpha$. Quantitatively, the interaction can be expressed as: $P = \alpha \mathbf{E}$, where $P$ is the transient dipole moment induced by the oscillating electric field $\mathbf{E}$. This periodic interaction of the molecule and the electromagnetic radiation from laser source and sets the molecule in vibration. Thus, when a monochromatic light source with frequency, $\nu_0$, interacts with a molecule, it turns them into vibrating dipoles with a frequency $\nu_m$. The excited molecules or the vibrating dipole reemit the light, which may be of three different frequencies depending upon the prior state of the molecule and accordingly divided into three following cases (schematically shown in Fig. 3.6):

1. when a monochromatic radiation interacts with a molecule at a ground level ($\nu=0$), it is excited to a virtual state which is not an eigen function of the molecule. From the virtual state the molecule may come back to ground state by emitting radiation of same wavelength as it had absorbed. This is known as Rayleigh scattering.

2. The excited molecule may drop to $\nu=1$ vibration level, then the scattered radiation will be less in energy by a quantity which is the difference of energy between $\nu=1$ and $\nu=0$ vibrational levels. Thus the energy of the scattered radiation will be $h\nu_0 - h\nu_m$, where $h\nu_m$ is the energy difference between $\nu=1$ and $\nu=0$ vibrational levels. This is called as “Stokes lines”.

3. If the molecule is excited from an initial state of $\nu=1$, then from the virtual state, it will come to ground level ($\nu=0$) and the scattered radiation will be of greater energy than the incident radiation. The energy of scattered radiation will be $h\nu_o + h\nu_m$. Since at room temperature the vibrational level $\nu=1$ is populated than $\nu=0$, the intensity of anti Stokes lines will be less than that of Stokes lines.
Fig. 3.6: Diagrammatic Illustration of Rayleigh and Raman scattering

The probability of Raman scattering is very less, say less than 0.001%. Such weak signal will be futile for the purpose of material characterization. Special measures should be taken to clearly observe the spontaneous inelastic Raman scattering in midst of the prominent Rayleigh scattering. Prior to the advent and development of lasers, intense source used to enhance the Raman signal, mercury arc lamps were used. Mercury arc lamps not only being intense but energetic as well used to decompose many of the systems. Modern Raman spectrometers are equipped with special components such as notch filters, tunable filters, laser stop apertures to ensure good quality Raman signal. Typically a Raman spectrometer consists of four basic components:

1. Excitation source (Laser)
2. Sample illumination system and light collection optics.
3. Wavelength selector (Filter or Spectrophotometer).
4. Detector (Photodiode array, CCD or PMT).

First, the sample is illuminated or excited with a laser source working (UV), visible (Vis) or near infrared (NIR) range. The signal due to reemission of photon or the scattered light is collected using a lens and filtered via generally a “notch” filter, which is actually a interference or a holographic grating. The real problem in getting only the signal due to Raman scattering is not due to the intensity of Raman scattering but due to noise in signal
because of stray light from the prominent Rayleigh scattering. The notch filters either in form of interference or holographic selectively removes the signal in the range of incident frequency. In older Raman spectrometers, photomultiplier tubes were used for detection of scattered photon, which used to make the measurement long. Newer generation of Raman spectrometers use multi-channel detectors like Photodiode Arrays (PDA) or, more commonly, a Charge-Coupled Devices (CCD) to detect the Raman scattered light, which are more sensitive and rapid in their operation.

In this work, a Jobin Yvon – LABRAM HR micro Raman spectrophotometer (Fig. 3.7), with excitation from 488 nm wavelength Ar ion laser source operating at 10 mW/cm² power in the range of 200 – 400 nm is used for confirming a particular crystallographic phase.

![Micro-Raman spectrophotometer](image)

*Fig 3.7: Micro-Raman spectrophotometer (Jobin Yvon – LABRAM HR) used in present study*

### 3.4 Compositional Characterization

#### 3.4.1 Energy Dispersive X-ray Spectroscopy (EDS) [5,6]

Energy Dispersive X-ray Spectroscopy (EDS), is a analytical technique used for elemental analysis of a sample. When a high energy electron (or sometimes X-rays) is incident on sample, electron present in core level of the atoms in the sample gets knocked off, leaving a core hole behind. This hole is then occupied by an electron from higher level, emitting a photon corresponding to the energy difference between the levels. This generally corresponds to X-ray region. As the atomic structure of each element is different, characteristic X-rays spectrum emitted by an atom in a sample will be different. This unique nature of X-ray spectrum of an element forms the basis of elemental analysis by EDS. Generally, EDS detectors are integrated in SEM or TEM, using the electron
source of the basic instrument. Mostly detectors are Si (Li) channels cooled by a cryogen for eg. liquid nitrogen or newer detectors include silicon drift detectors which can be simply cooled by Peltier cooler. This detector work on the ionization of detector crystal atoms to release free electron in the crystal upon incidence of X-rays. These free charge carriers produce electrical charge bias, which under the potential difference of detector get converted to electrical pulses. Thus converting the energy of X-rays into electrical pulses of corresponding size. Different electrical pulses correspond to different elements. As X-ray emission from each element’s atom occur irrespective of other, spectrum can be measured for entire energy range revealing signals for all the elements present independently.

EDS yields qualitative as well semi-quantitative information about the element present in the sample. EDS has the advantages of being faster than most of the analytical tools. When collecting the data in spot mode information about presence of different element in the sample can be obtained in few seconds. While in semi-quantitative mode the relative elemental concentration can be obtained from the relative peak intensity ratio. EDS also have the strength in terms of ease of sample preparation and sample loading.

However, accuracy of EDS is limited by nature of sample. Problem arises if the sample consists of elements which have overlapping characteristic X-ray peaks. Signal reaching the EDS detector is X-ray emitted by all atoms excited by incoming electrons. Although, X-ray emission occurs isotropically, thus it is possible that these emitted X-rays do not reach the detector. The X-ray reaching detector is thus dependent on the energy of X-ray emitted and density of sample. The EDS detectors are fitted with beryllium windows, are theoretically capable of analyzing all the elements upto Uranium. But in general the response for lighter elements differs from that of heavier elements, as the ionization cross-section each element differs. Also, absorption of the emitted X-ray and secondary fluorescence due to emitted X-rays also affect the detectivity. Thus corrections for these sources of errors is applied and is called as ZAF (Z – atomic number, A-Absorbance, F-Fluorescence) corrections.

The EDS in this thesis are acquired with the aid of Jeol JSM-5610 LV SEM with OXFORD EDS detector. The samples are mounted as such without any carbon coating.
3.4.2 X-ray Photoelectron Spectroscopy [7,8]

X-ray photoelectron spectroscopy (XPS) is surface sensitive elemental analysis tool. XPS involves bombarding the sample surface with monoenergetic soft X-rays and analyzing the energy of electrons thereby emitted. These X-ray photons have limited penetrating power, making XPS a surface sensitive tool. The principle of XPS is the emission of photoelectron from material surface upon shining light of appropriate wavelength. Mathematically, the photoelectron emission is governed by Einstein relation as:

$$h\nu = K.E. + B.E. \quad \ldots\ldots \quad (3.5)$$

where, $h\nu$ is the energy of incident photon, K.E. and B.E. are kinetic energy and binding energy of ejected photoelectron, respectively. Binding energy of the emitted electron is given by the difference between the initial and final states of electron. Depending upon the orbital, the binding energy of the electron differs and hence the kinetic energy of the ejected electron. Number of final states are possible forming a spectrum, since the atomic structure of each element differs. The intensity of the signal is governed by the cross-section or probability of ionization process. By definition, Fermi energy level is assigned zero binding energy. Because every element has a unique set of binding energies, rendering XPS to be elemental analysis tool. The slight change in the binding energies arise cause of the chemical potential and polarizability of the compound. XPS thus can be used to evaluate, qualitatively the chemical state (from binding energy) and quantitatively the relative concentration of element in a given sample surface. In a multicomponent sample the spectrum is approximately the sum of peaks due to individual elements.

![Diagram](image.png)

*Fig 3.8: Illustration of Photoelectron emission and Auger electron emission*

Apart from the ejection of photoelectron the other competing phenomena is of Auger electron emission. After ejection of a photoelectron due to incident X-ray photon, a
vacancy is created in core level. This vacancy is occupied by an electron from higher level and a second electron is simultaneously emitted taking away the excess energy. This second electron is called as Auger electron, and has kinetic energy equal to energy difference between the initial ion and final doubly charged ion. The emission of Auger electron occurs irrespective of mode of initial ionization. Emission of Auger electron occurs within $10^{-14}$ s after ejection of photoelectron. Thus, generally the ionization due to X-ray photon leads to emission of two electrons – photoelectron and Auger electron. The sum of the kinetic energies of the photoelectron and Auger electron cannot be greater than the energy of ionizing photons. Fig. 3.8 illustrates both photoelectron and Auger electron processes.

Since electron is a charged particle, it interacts strongly with matter. Thus, however the X-ray photons may ionize the atoms up to a depth of few microns under the sample, only the electrons originating from about few nanometers underneath sample can leave the sample surface elastically. The elastically ejected electrons form the peak in XPS spectrum. Whereas, the electrons originating from much below the surface lose energy while approaching the surface and form the background in XPS spectrum.

Principle components of an X-ray photoelectron spectrometer include

1. An X-ray gun generally dual source using Al K$\alpha$ (1486.6 eV) and Mg K$\alpha$ (1253.6 eV).
2. A vacuum chamber, where the sample is placed for measurement
3. X-ray monochromator
4. Electron energy analyzer
5. Ion gun for cleaning the sample surface

Depending upon the type of sample, field of interest and study to be carried out, different sample protocols are popular. Powder samples are simply dusted lightly on an adhesive medium or mechanically made stuck to the sample holder. If the absorbed substance is not study of interest, the sample is washed with suitable solvent and dried before run. Often mechanical means of exposing a fresh sample surface, such as cutting, abrasion etc. are carried out in a vacuum chamber or under inert atmosphere just before measurement. Powder used for measurement are crushed slowly (to avoid any changes due to the subsequent heat generated) to obtain fresh surface. Frequently, the samples are sputtered with ion (generally Ar$^+$) to remove any undesirable surface impurity for eg. native oxides, formed due to exposure of atmosphere.
All the measurements are carried out under ultra high vacuum, UHV (< 10⁻⁹ torr.). Since all the measurements of K.E. of emitted photoelectrons are done with respect to the work function of analyzer (Φ), the equation can be written as:

\[ hν = K.E. + B.E + Φ \quad \ldots \ldots \quad (3.6) \]

The electrons leaving the sample are detected by an electron spectrometer according to their kinetic energy. The analyzer is usually operated as an energy window, referred to as the pass energy, accepting only those electrons having energy within the range of this window. To maintain a constant energy resolution, the pass energy is fixed. Incoming electrons are adjusted to the pass energy before entering the energy analyzer. Scanning for different energies is accomplished by applying a variable electrostatic field before the analyzer. This retardation voltage may be varied from zero up to and beyond the photon energy. Electrons are detected as discrete events, and the number of electrons for a given detection time and energy is stored and displayed. Generally, scans are performed in two different modes (i) survey scans (0-1400 eV for Al Kα and 0-1200 for Mg Kα) greater pass window of generally ~ 45 eV for determining the all possible elements present and (ii) Detail scans, a higher resolution scan with usually a pass window of ~ 20 eV, of a particular chemical state required for quantitative analysis purpose.

Instrument is calibrated using standards, the binding energy of certain chemical state of which are well agreed upon. Generally, Cu 3p (Al Kα: 75.13 eV, Mg Kα: 75.14 eV), Au 4f7/2 (Al Kα: 83.98 eV, Mg Kα: 84.00 eV), Ag 3d5/2 (Al Kα: 368.26 eV, Mg Kα: 368.27 eV), Cu L3MM (Al Kα: 567.96 eV, Mg Kα: 334.94 eV), Cu 2p3/2 (Al Kα: 932.67 eV, Mg Kα: 932.66 eV), AgM4NN (Al Kα: 1128.78 eV, Mg Kα: 895.75 eV) XPS lines are used for calibration purpose.

Insulating sample may acquire charge due to photoionization. This causes shift of binding energies. Thus before analysis the data is corrected for errors due to sample charging with respect to the peak due to adventitious carbon (284.6 eV).

3.4.2a Quantitative element determination

Number of photoelectron emitted per second in specific spectrum peak i.e. the intensity of the peak, is given by:

\[ I = n.f. \sigma. θ.v. \lambda. A. T \ldots \ldots \quad (3.7) \]
where, $n$ is the number of atoms of the element per cm$^3$ of the sample, $f$ is the x-ray flux in photons/cm$^2$-sec, $\sigma$ is the photoelectric cross-section for the particular atomic orbital of in cm$^2$, $\theta$ is an angular efficiency factor for the instrumental arrangement based on the angle between the photon path and detected electron, $y$ is the efficiency in the photoelectric process for formation of photoelectrons of the normal photoelectron energy, $\lambda$ is the mean free path of the photoelectrons in the sample, $A$ is the area of the sample from which photoelectrons, are detected, and $T$ is the detection efficiency for electrons emitted from the sample. Thus, number of atoms of the element per cm$^3$ can be expressed as:

$$n = Lf \cdot \sigma \theta y \lambda A T$$  \hspace{1cm} (3.8)

The denominator of this expression is defined as atomic sensitivity factor (S).

Assuming a atomic sensitivity factor to be matrix independent, a general equation for estimating relative ratios of two elements can be written as:

$$n_1/n_2 = (I_1/S_1)/(I_2/S_2)$$  \hspace{1cm} (3.9)

where, $I_1$ and $I_2$ are intensities of strong lines of the respective elements. Though the quantities $\sigma$ and $\lambda$ vary from material to material but their ratio remain constant. Thus, for any spectrometer, it is possible to develop a set of relative values of $S$ for all of the elements. Multiple sets of values may be necessary for instruments with multiple x-ray sources at different angles relative to the analyzer.

A general expression for determining the atom fraction of any constituent in a sample, $C_x$, can be written as an extension of equation:

$$C_x = n_x/\Sigma n_i = (I_x/S_x)/(\Sigma I_i/S_i)$$  \hspace{1cm} (3.10)

The values used in this work are based on empirical values are due to Wagner et al. [8]. X-ray photoelectron spectroscopic study in this work is carried out using a VSW Spectrometer (Fig. 3.9), employing Al $K\alpha$ (1486.6 eV) as the incident radiation source. The analyzer work function is determined by assuming the binding energy for Ag3d$\text{5/2}$ peak to be 367.9 eV. On considering Ag3d$\text{3/2}$ peak as reference, the binding energy of adventitious C1s peak on standard silver sample surface is 284.6 eV. All binding energies are referred to carbon 1s peak for sample charging. Before performing the scan, the sample is rinsed with methanol and dried in air. Also, the sample is sputtered with 200 eV Ar$^+$ ions for 5 mins. to remove any impurity due to atmospheric exposure. A significant reduction in the intensity of adventitious C 1s peak is observed after sputter cleaning.
3.5 Morphology and surface topography

3.5.1 Electron Microscopy [5,6]

Microscope is an instrument which magnifies the features of an object beyond the visibility of normal human naked eye. The capability of a microscope is primarily reflected in terms of the resolution of the microscope; resolution is the smallest distance between two distinguishable points. Classically, the resolution is defined by Rayleigh’s criteria: \(0.61\lambda/\mu\sin \beta\), where \(\lambda\) is wavelength of the projectile, \(\mu\) is refractive index of the medium, \(\beta\) is the semi angle of lens. Resolution of optical microscopy is thus, limited theoretically to \(\sim 300\) nm (assuming \(\mu\sin \beta\), the numerical aperture to be 1 and wavelength of 550 nm, i.e. green light).

de-Broglie proposed that electron can behave as wave as well as particle, with its wavelength given as: \(\lambda\) (nm) \(\sim 1.22/E^{1/2}\). To illustrate, a 100 keV electron has wavelength of 4 pm, thus it follows using an electron as projectile can lead very high resolution by accelerating the electron desirably (theoretically!). Electron microscopes have the capabilities far exceeding that of optical microscopy with respect to their resolution and depth of field.
Electron is a charged particle with mass of $9.11 \times 10^{-31}$ kg. When a high energy electron impinges on a sample, number of signals arises from the specimen, giving different information about the sample qualitatively and quantitatively (Fig. 3.10). This has lead to development of different analytical tools. By far the most common being the Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

![Diagram of electron interactions](image)

**Fig. 3.10:** (Left) Different signals generated from sample upon the incidence of high energy electron beam, picture the depth profile of these signal

### 3.5.1a Scanning electron microscopy

Scanning Electron Microscopy, SEM utilizes the incoherently backscattered electrons (or simply backscattered electrons), secondary electrons, characteristic X-rays or visible light (cathode luminescence) signals from the sample. Most commonly, the backscattered electron or secondary electrons are used. The basic instrumentation of SEM consists of electron source employing thermoionic emission from tungsten or LaB$_6$ filament or Field emission gun. The SEM mainly is used to study the surface topography of sample, for eg. morphology of particles or films, also thickness of films. Depending upon the accelerating voltage (or energy of electrons) and intensity of source, the magnification of a SEM can vary over 6 order of magnitude from 10 to $\sim$ 500000. The resolution of a SEM can go down as much as $20 - 1$ nm, generally varying from instruments. In a SEM the electron beam is scanned over sample in raster fashion and the scattered electrons are collected by secondary electrons or back scattered electron detector. The energy of primary electrons from the source is in general limited to 1-30 keV to limit the interaction volume of sample that will generate the signal. Low energy primary electrons provide high sensitivity to surface of samples. Resulting low energy secondary electrons can be easily collected by positively charged detector. Most common secondary electron detector is Everhart-Thomley detector, consisting of a positively
charged grid attracting the secondary electrons and then accelerating them to produce a light pulse on a scintillation screen. This light pulse is then amplified by a photomultiplier.

Samples for SEM should be electrostatically conducting; otherwise sample charging can occur due to ionization from electron beam. In case, sample is not inherently conducting, sample is first coated (~ 1 nm thickness) with conducting and inert substance eg. gold, platinum, graphite etc.

Scanning Electron Micrograph used in this study is Leo 440i (Fig. 3.11). The samples prior to scans are gold coated. During the scans only secondary electrons detector is used.

Fig 3.11: Scanning Electron Microscope (Leo, 440i) used in present study

3.5.1b Transmission electron microscopy [9]

Transmission Electron Microscopy, TEM is a type of electron microscopy which analyzes the electron which pass through a ultra thin sample, generally with thickness around tens of nanometer. In principle, the sample thickness is less than or almost about the mean free path of primary electrons. Electrons emitted from the source are first accelerated to energy of about few hundreds of keV. This accelerated beam of electrons is allowed to pass through the sample. Since the signal is due to transmitted primary electrons, the electrons can be accelerated to few hundreds of keV without any problem in resolution, which although a issue for secondary electrons in SEM. These electrons while passing through the sample get scattered in different ways. Generally, the TEM is operated in two modes i.e. imaging and diffraction. The imaging mode evaluate/ displays
the spatial distribution and diffraction mode collects the angular distribution of the transmitted electron intensity. The ray diagrams for the both the modes is shown in Fig. 3.12. The electron microscope in general have special kind of lenses converging or diverging the electron beam by electromagnetic fields. In TEM specifically the electron optics is optimized for higher current densities by reducing the distance between the two objective lenses. Magnification as high as 500 kX is usual in TEM. In principle, there are number of imaging modes: Bright field, dark field, phase contrast, electron energy loss. Most popular being bright field and phase contrast (also called as high resolution Transmission Electron Microscopy). High resolution TEM utilizes field emission source producing coherent electron beam with high intensity and small energy spread. This particular mode exploits the interference of electron wave with itself from the imaging plane. As such, only amplitudes of electron waves can be recorded, however for HRTEM, microscopic aberrations are manipulated to convert the phase of electron wave to amplitude which then can be recorded.

Samples commonly are prepared on conducting metal grid which aids in accelerating the electrons as becoming the counter electrode as well as allows the beam to pass through it. The Transmission Electron Microscopy of samples in thesis is done with Jeol, JEM 2100 TEM in Bright field, Phase contrast and diffraction modes. Sample is loaded as such without any prior treatment.

![Ray diagram of Imaging and Diffraction mode in TEM](image)

Fig. 3.12: Ray diagram of Imaging and Diffraction mode in TEM
3.5.2 Atomic Force Microscopy [10]

Atomic force microscopy (AFM), is a part of scanning probe microscopes. The first of this line is scanning tunneling microscope (STM). However, STM is restricted to electrically conducting surfaces. AFM is a tool used for imaging, measurement and manipulation at nanoscale. AFM, unlike electron or optical microscopy, does not utilize electron or photon to image the sample. In a non-technical sense, optical and electron microscope “see” the object and amplify it whereas AFM “feels” the object. In an AFM the image forms due to the inter atomic/frictional forces such Van der Waal, electrostatic forces or Casimir forces etc., which become significant when two object are brought too close. In particular, AFM basically consists of a cantilever (with length of around 100 μm) having a sharp tip, with tip cross section of few tens of nanometer, which acts as test probe. When this tip is moved close to surface of the sample, a deflection of cantilever is produced because of the forces being active due to the proximity. This deflection produced in the cantilever due to strain, obeys the Hooke’s law. The deflection of the tip is measured by reflection of laser beam from the back of the tip. The reflected beam is then collected by a position sensitive photodetector. The position sensitive detector consists of a close spaced photodiode couple connected to differential amplifier. Noting the change in intensity from one spot to other, deflection of cantilever is converted into electrical signals. The image of the surface is obtained by scanning the tip over the surface in raster fashion. AFM have three prong advantages over TEM or SEM: (i) it covers the scan range from that of optical microscope till almost that of TEM and (ii) unlike 2-diminsional imaging from SEM, AFM provides 3-dimensional information about the surface of the sample, (iii) no special sample preparation is required, like for SEM and TEM. Also, the conditions for scan are not limited for eg. vacuum or gas environment. Only negative point is that more time is taken for the scan. The AFM can be operated in different modes depending upon type of sample and application. Some of these are: Contact mode, Non-contact mode (NC-AFM, close contact mode, FM-AFM), Intermittent Contact mode (IC-AFM, AM-AFM, Tapping) Chemical Force Microscopy (CFM) Lateral Force (LFM, FFM)) (STS), Electric Force (EFM), Force Microscopy, Nanoindentation Magnetic Force (MFM), Kelvin Probe (KPM, SKPM), Scanning Thermal Microscopy (SThM), Nano oxidation Lithography, Dip-pen Nanolithography (DPN). The typical components of a AFM are shown in Fig. 3.13.
In this work the scans are done in non-contact mode only using Nanosurf, EasyScan 2 Atomic Force Microscope (Fig. 3.14). In this mode, the cantilever tip does not come in contact with sample surface. Rather the cantilever is made to oscillate at its resonant frequency or little above, while amplitude of oscillation typically ranges from 10 nm to as low as few picometers. In the proximity of sample (up to ~ 10 nm), van der Waals forces or other long range forces become dominant. These forces act to alter the oscillation frequency of the cantilever from its resonant frequency. The change in the oscillation is supplied to a feedback loop which adjusts the distance between the tip and sample so as to keep the oscillation frequency equal to the resonance frequency of the cantilever. This continuous measurement of distance from a point on the sample surface and the tip of the cantilever allow the AFM software to form an image encoding the topography of sample. As there is no physical contact made between the sample and tip, the tip or sample does not undergo any degradation like in contact mode.

Fig 3.14: Atomic Force Microscope (Nanosurf, EasyScan2) used in present study
3.6 Optical Characterization

3.6.1 UV-Visible-NIR spectroscopy

The region of UV-Vis-NIR in the electromagnetic spectrum corresponds to energy difference between the valence and conduction bands. Also, the radiation from sun on earth lies in this region only; therefore it is of great importance to study the UV-Vis-NIR spectrum of materials meant for solar cell application.

UV-Vis-NIR spectroscopy corresponds to electronic transitions between the upper most filled energy levels to lower most unfilled energy levels. Thus to understand the optoelectronic behaviour of a solar cell material, it is crucial to study UV-Vis-NIR spectrum. The measurement of UV-Vis-NIR spectrum include irradiating a sample with a monochromatic light and measuring the transmittance (the leftover light) and reflectance at a fixed angle (specular) or overall (diffuse). To see, optical measurements are one of simplest of all and all the parameter are linearly additive.

A UV-Vis-NIR spectrophotometer consists of following basic components

i. a light source – generally, tungsten bulb covering mostly the visible to NIR region and deuterium lamp mainly for UV region.

ii. a monochromator – since the emission from a light source is polychromatic and is actually a distribution of wavelengths with different intensities, a monochromator is required to sort a particular wavelength at a time. Grating is mostly employed as monochromator, which works on the principle of interference.

iii. sample cell – to hold a liquid (cuvetts), solid including film samples

iv. Detector – to measure the transmitted or reflected light. Often, photomultiplier tube, PMT (~ 165-1000nm) and photoconducting PbS (~ 1600 – 3300 nm) plus InGaAs (~ 700- 1800 nm) detectors are utilized for detection in UV-Vis and IR range, respectively.

Along with this there are other components including electronics and auxiliary optics components such as slits, beam splitter etc.

Mostly, a double beam spectrophotometer is used, with reference as well as sample cells. The reference cell is used to cut-off any absorption due to solvents or due to substrates in case of films. Since the distribution of radiation from the light source and response of detector are not “flat”, therefore a blank measurement is performed to record
the maximum intensity at a particular wavelength. This operation is called as “baseline correction”.

Optical spectrum of semiconductor consists of number of phenomena, however three of the following stated below will be most pertinent to the present work:
(i) fundamental absorption, (ii) absorption due to defects and (iii) exciton absorption.
Fundamental absorption is the most prominent of the three, is due to the electronic transition from the valence to conduction band. The transition probability is dependent on density of states. However, on the basis optical absorption a semiconductor can be categorized in direct and indirect band gap material. In direct band gap the maximum of conduction band and minimum of valence band lie at same k – value, whereas at different k values in an indirect band gap material. The transition in indirect band gap material, otherwise forbidden (Laporte selection rule: conservation of momentum), becomes possible due to assistance of phonons (managing the difference of momentum). Thus, transition probability of electronic transition due to fundamental absorption is low (governed by the collision probability of proper phonon to the excited electron). The band gap of polycrystalline can be extracted using the Tauc relation:

\[(\alpha h\nu)^n = A(h\nu - E_g) \quad \ldots \ldots \quad (3.11)\]

where, \(\alpha\) is the absorption coefficient, \(n\) is a index depending upon type of transition whether indirect or direct. Theoretically, at the band gap of semiconductor (given sufficient thickness as per its absorption coefficient) the entire incident light with photon energy above its band gap, should be absorbed leading to sharp step in the optical spectrum. However, this is seldom a case especially in a polycrystalline (including nanocrystalline and microcrystalline) material. Often the absorption continues in region above band gap, causing a tailing feature in the spectrum. This absorption is essentially due to transition to and from the defect states. Lastly, there is certain absorption observed especially in case of nanocrystalline semiconductor belonging to photon energies below band gap. This absorption is caused by creation of a electron-hole pair, termed as exciton, upon absorption of light. The energy states due to formation of exciton exist just below conduction level and show sharp localized state like absorption behaviour. In this study, Shimadzu, UV-3600 UV-VIS-NIR spectrophotometer (Fig. 3.15) in wavelength range 400-2400 nm. Both Transmittance and specular reflectance modes have been utilized to study the optical properties of CTS thin films. The specular reflectance of films is normalized with respect to the reflectance of front coated Al mirror. Optical properties of
CTS nanoparticles and powder have been studied employing diffuse reflectance mode using integrating sphere. The diffuse reflectance is normalized with respect to reflectance of barium sulphate.

![UV-VIS-NIR spectrophotometer](image)

**Fig 3.15**: UV-VIS-NIR spectrophotometer (Shimadzu, UV-3600) used in present study

### 3.7 Chemical mechanism

#### 3.7.1 Thermal Analysis [11]

Thermal analysis techniques are those in which the a physical property of a substance or its reaction products is measured as a function of temperature. Usually, the substance is subjected to a controlled temperature program during the analysis. Although there are different thermal analysis tools, Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) are among two most popular thermal analysis techniques.

#### 3.7.1a Thermogravimetric analysis (TGA)

In a thermogravimetric analysis the mass of a sample in a controlled atmosphere is recorded continuously as function of temperature or time, as the temperature of sample is increased. The plot of mass or mass percentage as a function of time is called a thermogram or a thermal decomposition curve. The instrument consists of four basic components:

1. a sensitive microbalance, called as a thermobalance.
2. a furnace
3. a purge gas system for providing an inert, or reactive atmosphere

4. a computer system for instrument control, data acquisition and data processing

Thermobalances are available in different design from different manufacturer and are capable of quantitative measurement of sample mass ranging from 100 mg to less than 1 mg, generally ultimate mass detectivity of these balances can go up to 0.1 µg. The sample holder portion of the balance can be housed in the furnace, whereas the rest the portion of the balance remains thermally isolated from the furnace. The change in the sample mass causes actuation of a shutter system between a laser beam source and one of the photodiode pair. This result in a differential current output, which is then amplified and fed to a coil placed between the poles of a permanent magnet. The amplified photodiode current is monitored and transformed in terms of mass or mass loss information by the data processing system.

Furnaces typically can work in a temperature range of ambient to 1373 K or sometimes 1873 K. Heating rates can be varied from 0.1 K/min. to 100 K/min. The furnaces are well insulated to protect the balance. Provision for inert or reactive atmosphere is done within the furnace by different gases. The temperature axis is usually calibrated by a ferromagnetic material with known Curie temperature. The standard sample is suspended in magnetic field. Due to the magnetic interaction and the balance indicates an apparent mass. Upon heating, ferromagnetic to paramagnetic transition takes place at the Curie temperature and sample loses its apparent magnetic mass.

Sample holder is made of different materials optimized for different application and cost. Generally, sample holders in form of a pan of different capacities are made of Aluminium, Alumina or Platinum are available.

3.7.1b Differential Scanning Calorimetry (DSC)

In a DSC, a sample and reference are placed in holders in the instrument. Heaters either ramp the temperature at a specified rate or hold the DSC at a fixed temperature. The instrument measures the difference in the heat flow between the sample and the reference. There are three different types of DSC: (i) power-compensated DSC, (ii) Heat-flux DSC and modulated DSC. Each yields a plot of power or heat flow versus temperature.

In a power-compensated DSC, the temperatures of the sample and reference are kept equal to each other, while temperatures of both sample and reference are increased
or decreased linearly. The power needed to maintain the sample temperature equal to the reference temperature is measured. In a power compensated DSC, two separate heating units are employed to heat the sample and reference, individually. Temperature at the sample and reference side is measured with a platinum resistance thermometer. Instrument records power difference needed to maintain the sample and reference at the same temperature as a function of the programmed temperature.

In a heat-flux DSC, the difference in heat flow into the sample and reference is measured while the sample temperature is changed at a constant rate. Both sample and reference are heated by a single heating unit. Heat flows into both sample and reference material via an electrically heated constantan thermoelectric disk. Small aluminum sample and reference pans sit on the raised the constantan disk. Heat is transferred through the disks and up to the material via the two pans. The differential heat flow to the sample and reference pans is monitored by Chromel-constantan area thermocouples formed by the junction constantan platform and Chromel disks attached to the underside of the platforms. The differential heat flow into the two pans is directly proportional to the difference in the outputs of the two thermocouple junctions. The sample temperature is estimated by the Chromel-alumel junction under the sample disk.

Modulated DSC (MDSC) uses the same heating and cell arrangement as the heat-flux DSC method. In MDSC, a sinusoidal function is superimposed on the overall temperature program to produce a micro-heating and cooling cycle as the overall temperature is steadily increased or decreased. Using Fourier transform methods, the overall signal is mathematically deconvoluted into two parts, a reversing heat flow signal and nonreversing heat flow signal. The reversing heat flow signal is associated with the heat capacity component of the thermogram, and the nonreversing heat flow is related to kinetic processes. Usually, step transitions, such as the glass transition, appear only in the reversing heat flow signal, and exothermic and endothermic events may appear in either or in both signals.

In this work a combine TGA-DSC instrument from Mettler-Toledo, TGA/DSC 1 (Fig. 3.16) under static air in the temperature range of 323-1273 K at heating rate of 10 °C/min is used. The calibration in different temperature ranges are done by ascertaining melting points of well known metals: Indium, Aluminum, Gold. The measurements are carried out in air atmosphere at an heating rate of 10 K/min. The type of DSC incorporated in this instrument is Heat-Flux DSC. In a heat flux DSC, total heat flow, dH/dt can be expressed as:
\[ \frac{dH}{dt} = C_p(dT/dt) + f(T,t) \quad \ldots \quad (3.12) \]

where, H is the enthalpy in Jmol\(^{-1}\), \(C_p\) is the specific heat capacity in JK\(^{-1}\)mol\(^{-1}\), and \(f(T,t)\) is the kinetic response of the sample. Thus a Heat-Flux DSC thermogram includes signal due to heat capacity changes as well as kinetic (exothermic and endothermic changes) response.

![TGA/DSC instrument (Mettler-Toledo, TGA/DSC 1) used in present study](image)

**Fig 3.16:** TGA/DSC instrument (Mettler-Toledo, TGA/DSC 1) used in present study

### 3.7.2 Infrared Spectroscopy [12]

When a molecule is irradiated with infrared radiation, the molecule undergoes transition between the vibrational and rotational levels. However, these transition are quantized and the vibrational-rotational spectrum of molecule is dependent on its structural features and its environment such as bonding overlap, atomic mass, molecular geometry etc. Thus, vibrational spectrum of each molecule under different environment is unique.

The bonds in a molecule are non-rigid and behave, in classical sense, as springs. Vibrational motion of a molecule involves periodic and transient change of bond distances, bond angles and dihedral angle about a equilibrium value for the ground state of molecule. Basically there are only two types of vibration in molecule: (i) stretching and (ii) bending. The stretching vibrational motion can be divided into: (a) symmetric and (b) asymmetric stretching, whereas bending mode can be sub-divided into: (a) in-plane bending including rocking and scissoring, and (b) out-of-plane bending including twisting
and wagging modes. These basic modes of vibration are schematically described in Fig. 3.17.

![Diagram of molecular vibrations](image)

**Fig. 3.17: Schematic demonstrating fundamental modes of vibrations of water molecule (plus and minus sign denote out of plane projection and do not represent any charge on the atoms)**

These basic modes of vibration in a molecule are also called as fundamental modes of vibration and their number for a molecule can be calculated from the number of vibrational degrees of freedom for a molecule. Thus for a molecule consisting n atoms, there are in all 3n degrees of freedom. For nonlinear molecules, three degrees of freedom describe rotation and three describe translation; the remaining 3n - 6 degrees of freedom are vibrational degrees of freedom or fundamental vibrations. Linear molecules have 3n - 5 vibrational degrees of freedom, for only two degrees of freedom are required to describe rotation.

For a particular mode of vibration to be “IR active”, it is required that during that vibration, the dipole moment of the molecule must change (gross selection rule). The specific selection rule (restriction due to quantum mechanical nature) for IR spectroscopy is that only a change of ± 1 in vibrational quantum number is allowed and are called as normal modes of vibrations. Occasionally, transition with vibrational quantum number change greater than ± 1 occur, though with low intensity and such transition are known as overtone vibrations. Beside these there are bands in spectrum arising at combination and difference of fundamental frequencies. Therefore the number of bands in the spectrum of a molecule are only seldom equal to number of vibrational degree of freedom.

In this study a Thermo, Nicolet 6700 Fourier Transform Infrared (FT-IR) Spectrophotometer is used (Fig. 3.18). For measurement samples are first mixed with
KBr and pellets are made using a dye-punch. Scans are performed in range of 400-4000 cm\(^{-1}\) with resolution of 1 cm\(^{-1}\).

*Fig. 3.18: FT-Infrared spectrometer (Thermo, Nicolet-6700) used in present study*

### 3.8 Electrical measurements

#### 3.8.1 Electrical conductivity measurement [13,14]

One of the most basic electrical properties of any semiconducting thin film is the conductivity (\(\sigma\)). Mathematically, it is expressed in the measurable physical quantities such as Voltage (V), Current (I), and dimensions of film as:

\[
\sigma = \frac{(I/V)}{(l/A)} \quad \text{.........} \quad (3.13)
\]

where, \(l\) is the distance between the electrodes and \(A\) is cross-section area of film. The conductivity generally in units of Ohm\(^{-1}\)cm\(^{-1}\) or S/cm.

Following Drude’s theory, conductivity of a semiconductor can be described in terms of the carrier concentration and mobility of carriers as (for intrinsic semiconductor):

\[
\sigma = n_e \mu_e + p_e \mu_p \quad \text{.........} \quad (3.14)
\]

Where, \(n\) and \(p\) are electron and hole concentration respectively, \(\mu_n\) and \(\mu_p\) are electron and hole mobilities, respectively, and \(e\) is the electronic charge. Mobility is further explained as: \(\mu = (e \cdot \lambda)/(m \cdot v_o)\), where \(m\) is effective carrier mass, \(v_o\) is carrier velocity and \(\lambda\) is mean free path of the carrier.

Conduction in ideal, crystalline semiconductor takes place when the electrons get excited from valence band to conduction band, giving rise to free electrons in conduction band and holes in the valence band. At absolute zero temperature all valence electrons
will remain frozen to their cores, therefore are supposed to show nil conductivity. As the
temperature is increased, due to collision between phonons, arising from the thermal
lattice vibrations, and some electrons in valence band statistically will possess energy to
surpass the forbidden energy gap and transit to conduction band. Thus the carrier
movement in semiconductor is essentially dependent on temperature. The probability that
an electron will jump to conduction band is governed by the Fermi-Dirac statistics
(electron being a Fermion). However, with simplification at higher enough temperature
this probability is mathematically written as:

$$ A \cdot \exp(-\Delta E/kT) \quad \ldots \quad (3.15) $$

where, for an intrinsic semiconductor $\Delta E$ is half the energy of the forbidden gap, $A$ is
complex term which is atleast function of mean free path, $\lambda$ and is constant for single
crystalline sample at higher enough temperature, $k$ is the Boltzmann constant and $T$ is the
temperature. The conductivity of semiconductor (since conductivity is linearly
proportional to free carrier concentration), therefore is directly proportional to some
exponential function of temperature, $T$. Thus, conventionally the conductivity data is
plotted as $\ln \sigma$ versus $1/T$, for easier deduction of various parameters from a line graph
rather than a nonlinear graph.

An important concept in quantum mechanical interpretation of crystalline
semiconductor is the “Fermi level”. At any real temperature it is defined as the fictitious
energy level where probability of finding an electron is 50%. Everything in band theory
picture of semiconductor holds a physical interpretation with respect to this level only.
For an intrinsic semiconductor Fermi level lies exactly at the centre of conduction and
valence bands. Whereas, for an extrinsic semiconductor it lies nearer to one of bands (the
proximity directly depends on the extent of doping) : for n-type semiconductor it lies
closer to conduction band and for p-type semiconductor it lies closer to valence band.
Thus while discussing transport of carrier, the $\Delta E$ refers to the “activation energy”
required to excite the electron from Fermi level to conduction band (n-type or intrinsic) or
a hole from valence band to Fermi level (p-type or intrinsic). It is also implied from the
term that conduction will occur only if the thermal energy ($kT$) of the carriers is greater
than $\Delta E$. For an intrinsic semiconductor the activation energy ($\Delta E$) is half the forbidden
band gap energy ($E_g/2$) and vice-versa, it is a test for determination of intrinsic behaviour,
of semiconductor. Since the location of Fermi level is dependent on the type and extent
doping, finding $\Delta E$ therefore give an idea about the type and extent of doping. From the
plot \( \ln \sigma \) versus \( 1/T \) for a perfectly crystalline semiconductor, a sharp change in slope of the will be observed when the thermal energy of the carrier will be equal to the activation energy and magnitude of the slope will provide information about the doping of semiconductor. Such carrier transport is defined as thermally activated conduction.

For a purely crystalline semiconductor, there is no actual energy state existing between the conduction band and valence band. However, in the case of polycrystalline (including microcrystalline, nanocrystalline etc.) due to the presence of grain boundaries (a sort of defect) there is possibility of existence of states between the bands and are called as gap states. The density and nature of these gap states is dependent on length of grain boundaries (extent of crystallinity) and nature of defect present at these grain boundaries (type of structural defect, presence of foreign atom, charge etc.). These states play significant role in carrier transport in polycrystalline semiconductor. Since these states fall in between the Fermi level and bands, the gap assisted carrier transport show change in slope (\( \ln \sigma \) vs. \( 1/T \) plot) at values less than activation energy required for thermally activated transport. Often the temperature dependence is described in terms of inverse integral or fractional power rather than linear. At quite low temperature generally up to below boiling point of liquid nitrogen (77 K), conduction in such systems observes quantum mechanical phenomenon of tunneling known as variable range hopping (VRH) and show \( T^{0.25} \) dependence. In such cases carriers jump from one state to another irrespective of the energy difference. In intermediate temperatures, between VRH and purely thermally activated conduction, other fractional power laws for temperature dependence are observed, such as nearest neighbour hopping (NNH). Thus in nanocrystalline semiconductor, which lies in the purview of this thesis, the conduction over entire temperature range is described in term of combination of multiple conduction functional temperature ranges.

Also the pre-exponential factor depending on \( \lambda \) becomes a function of temperature, thus it becomes difficult to understand the temperature dependent carrier transport solely by studying variation in conductivity. Further to deduce various physically important parameter such as mobility, carrier concentration, location defect states and type of carrier scattering, it becomes essential to include other electrical measurements. In this study thermoelectric power has been used to study temperature dependent carrier transport in these nanocrystalline films of CTS. Thermoelectric power is alternative to more popular transport analysis technique, Hall measurement, especially
when conductivity of samples is low. It has been employed earlier to study the carrier transport of metal chalcogenide and oxide film and has been found to yield similar equivalent values for different semiconductor relevant electrical parameters [15].

In this thesis the electrical conductivity of CTS films is measured using two-probe D.C. conductivity measurement. As the contact resistance of the films is very low (<10³ Ohm) in comparison to film resistance, two-probe measurement method is accurate. The circuit for measurement of resistance of a particular sample consisted of a voltage source, the sample film and a standard resistance, connected in series. The current (I) in the circuit is calculated by measuring the potential drop across the standard resistance. The resistance of the sample (R_s) was calculated by measuring the voltage drop (V_s) across the sample and from the magnitude of the current (I). The circuit for measurement of sample resistance is shown in Fig. 3.19.

The conductivity of the film is determined using the length, width and thickness of the film via following relation:

\[
\text{Conductivity (}\sigma\text{) = } (1/R_s)(A/l)
\]

where, A is area of cross section given by thickness x width of the film and l is length of the film.

![Fig. 3.19: schematic of the circuit diagram for measurement of film resistance](image)

### 3.8.2 Thermoelectric power [14,16]

Thermoelectric power (TEP) refers to the e.m.f. generated between two differentially heated ohmic contacts on material. It is required that the e.m.f. must be measured with out flow of current, thus TEP is actually measured potentiometrically. TEP is dependent on the contact between the ohmic contact conductor (metal etc.) and semiconductor. Since the TEP of semiconductor is much greater than conductor, while measurement of TEP on semiconductor, TEP at contacts has negligible contribution. The TEP is significantly dependent on temperature and temperature difference must be maintained less than 10 K, while studying the temperature dependent carrier transport.
The sign and magnitude of TEP depends on the type and concentration of carriers. Apart from this, the TEP is greatly affected by type of scattering and is mathematically related to majority carrier concentration as:

\[ p = N_v \left[ A + \frac{S(\text{TEP})}{k/e} \right] \quad \ldots \ldots \quad (3.16) \]

where, \( p \) is hole concentration, \( S(\text{TEP}) \) is the thermoelectric power in units of \( \mu V/K \). \( A \) is constant due to scattering and varies between 1.8 to 4, \( N_v \) is the effective density of state for valence band and is given as:

\[ N_v = 2 \left( \frac{2\pi m_h^* k T}{h^2} \right)^{3/2} \quad \ldots \ldots \quad (3.17) \]

where, \( m_h^* \) is the effective mass of hole (0.1\( m_e \)), \( k \) is the Boltzmann constant, \( h \) is the Planck’s constant.

The equation holds for thermally equilibrated systems. Actual thermoelectric power quantitatively includes contribution from charge carrier movement and from phonon drag. Phonon drag contribution arises from preferential movement of phonons from the hot end to cold end. However, such contribution becomes negligible above liquid nitrogen temperature.

Thus a combination of thermoelectric power and conductivity over a temperature can essentially detail about temperature dependent carrier transport in nanocrystalline semiconducting thin films.

\[ \text{Fig. 3.20: Schematic of thermo-electric power measurement} \]
Since the materials concerned in this work are intended for solar cells, the study of carrier transport in presence of light becomes crucial for the purpose. For elucidating the mechanism of carrier transport of CTS films under dark and light, unique cryostat with inverted structure fitted with quartz window is fabricated. The cryostat is capable of measurement of electrical conductivity and thermoelectric power from down upto 120 K under dark and light conditions. The design enables easy sample loading with the help of pressure contacts fitted with “Type T” thermocouples (Copper-Constantan) for concomitant temperature measurements. Simultaneous data collection is done with the help of Rish Multi 18 S digital multimeter with RS 232 port enabled data acquisition system. The temperature gradient during the thermoelectric power is maintained with a PID controller. The Schematic of thermo-electric power measurement is shown in Fig. 3.20. The design and photograph of the cryostat along with data acquisition system is given in Fig. 3.22. For the purpose of Ohmic contacts colloidal graphite paint is used.

3.8.3 I-V characteristics of solar cells

A schematic for the measurement of current-voltage characteristics is shown in Fig. 3.21. A Keithley 2611- A source-cum-meter is used to apply voltage and measure the current flowing through the solar cell or Schottky barrier. The voltage is swept from 0.5 to 1 V in 0.01 V increments. The computerized control of the measurement and the data acquisition is done using Keithley lab tracer 2.0 software module.

![Solar cell Schematic](image)

**Fig. 3.21: Schematic of current-voltage measurement of solar cells**

Standard J-V measurements are done at 278 K under dark and under illumination using a solar simulator (Newport-Stratfort 150W, 96000) with simulated AM 1.5 spectrum and power density of 100 mW/cm².

The open-circuit voltage \( V_{OC} \) and short-circuit current \( I_{SC} \) of a solar cell is determined from the intersection points of J-V characteristics at voltage and current axis,
respectively. The series resistance ($R_s$) and shunt resistance ($R_{sh}$) of the cell is calculated from the slope of the J-V characteristics at voltage and current axis, respectively. The fill factor (FF) and power conversion efficiency of the cell is calculated using the following relations:

$$\text{FF} = \frac{V_{mp} \times I_{mp}}{V_{oc} \times I_{sc}} \quad \ldots \ldots \quad (3.18)$$

where, $V_{mp}$ and $I_{mp}$ are the values for the voltage and current at maximum power point.

Power conversion efficiency (PCE):

$$\eta = \frac{(V_{oc} \times I_{sc} \times \text{FF})}{(\text{Input power x cell area})} \quad \ldots \ldots \quad (3.19)$$
References


