Chapter II

Methods and Measurements

2.1. Introduction

There has been a lot of interest in semiconducting materials because their physical and chemical properties change rapidly with the particle size. These materials are attracting a great deal of attention due to their fundamental electronic and optical properties [1]. The physical, chemical and photo-electrochemical properties of such materials are mainly dependent on the methodology adopted for the preparation of the thin films [1-7]. The characteristics of thin film materials are very different from the bulk materials. Hence, it is necessary to select a proper preparation technique for the deposition of semiconducting materials in the form of thin films. Similarly, it is a common experience that the electronic and other properties of II-VI materials in thin film form are highly structure sensitive, which in turn severely influence the device performance [2-6]. Therefore, it is essential to characterize the semiconductor material thoroughly through its various properties prior to its use as a device element. This chapter deals with the experimental tools and techniques used in the various fabrication processes and characterization methods pertaining to the thin film materials under investigation.

2.2. Chemical Solution Deposition

A chemical solution deposition method (CSD), is also called as solution growth, controlled or arrested precipitation, electroless deposition, etc. Chemical deposition of thin films results from moderately slow chemical reaction that leads to the formation of
thin solid layer onto the immersed substrate surface at the expense of chemical reaction between the aqueous precursor solutions [2-13]. In this method, when cationic and anionic solutions are mixed together and if the ionic product exceeds or becomes equal to the solubility product, precipitation occurs as ions combine together on the substrate and in the solution to form nuclei [2-13]. Films can be grown on either metallic or nonmetallic substrates by dipping them in appropriate solutions of metal salts without the application of any electric field. Deposition may occur by homogeneous chemical reaction, usually reduction of metal ions, in a solution by a reducing agent. The growth rate and the degree of crystallinity depend upon the temperature of the solution. The main advantage of this method is to deposit the films on non-accessible surfaces such as rounded glass tubes. The chemical solution deposition is the simplest of the chemical methods and it has many advantages as [2-5, 7-13];

1. It is ideally suited for large area thin film depositions; substrate surfaces of both accessible and non-accessible nature could easily be deposited.
2. It is simple, inexpensive and does not require sophisticated instrumentation.
3. The deposition is usually at low temperature and avoids oxidation or corrosion of the metallic substrates.
4. Stoichiometry of the deposits can be maintained since the basic building blocks are ions instead of atoms.
5. Slow film formation process facilitates better orientation of the crystallites with improved grain structure.
6. Doped and mixed films could be obtained by merely mixing the dopant solution directly into the reaction bath.

7. Electrical conductivity of the substrate material is not an important criterion.

8. An intimate contact between reacting species and the substrate material permits pinhole free and uniform deposits on the substrates of complex shapes and sizes.

9. A wide variety of (conducting / non-conducting) substrate materials can be used.

10. Dissociation rate of organometallic complex to release free metal ions for reaction is well controlled by maintaining the pH of the reacting solution.

Chemical solution bath deposition method has been used for the formation of II-VI, III-V and IV-VI semiconducting thin films. Recently, we have successfully used the chemical bath deposition method for deposition of the Hg-Pb-S, Zn-Cr-Se, Hg-Cd-S, Cd-Co-S etc thin films [2-5, 7-13]. A traditional chemical deposition method was modified and attempts were made to make it more convenient, optimistic and an efficient system. A schematic diagram of a chemical solution deposition method designed and developed by us is displayed in fig. 2.1. The experimental set up consists of a dust proof chamber, an oil bath, a reaction vessel and a substrate holder.

2.2.1 A dust proof chamber

A dust proof metallic chamber was designed and fabricated with the dimensions 180 cm x 80 cm x 100 cm to provide the clean environment and to avoid contamination from dust particles, atmospheric gases, etc. An exhaust outlet at the top of the chamber was fitted to remove the gases evolved during the film deposition.
2.2.2 An oil bath

A paraffin oil bath with constant temperature arrangement, supplied by the Modern Industrial Corporation, Mumbai, was used to achieve the desired deposition temperature. A 2 kW electric heater was used to heat the paraffin oil within the accuracy range of ± 0.5°C. A synchronous universal motor was used for continuous stirring of the oil to maintain uniform temperature throughout the oil bath.
2.2.3 The reaction vessel

A reaction vessel was 250 ml capacity glass beaker in which appropriate quantities of the reacting solutions were mixed together. The beaker was then mounted in an oil bath by means of suitable home-made o-ring stand. The reacting mixture was then maintained at appropriate deposition temperature.

2.2.4 The substrate holder

The substrates were mounted on a specially designed ‘substrate holder’. Fig. 2.2 shows a schematic view of the substrate holder used for deposition of the materials. A substrate holder is a circular disc made up of bakelite material. The thickness of the substrate holder is 10 mm and the diameter is less than the diameter of the beaker (5cm) so that the substrates attached to substrate holder can move freely in the reaction mixture in a beaker. The disc was slotted to fix the substrates with the help of screws in such a way that each of the substrate is exactly perpendicular to the next. The continuous and proper

![Figure 2.2 Cross-section view of the substrate holder.](image-url)
churning of the solution in the reaction bath was therefore made possible that helped in the deposition of uniform films with a better orientation of the crystallites [2, 3, 7, 9-13]. The substrate holder was then fitted to a constant speed AC/DC gear motor so that the substrates can be rotated in the reaction mixture. The motor was mounted on a drilling machine stand. The stand was modified in such a way that the height of the motor can be properly adjusted. About 80% of the substrate area was immersed into the reaction mixture.

2.3 Synthesis of CoS and Co$_{1-x}$Zn$_x$S Thin films

2.3.1 The substrates

The substrates used for deposition of the thin films were non-conducting amorphous spectroscopic grade glass slides of the size 7.5 cm x 2.5 cm x 0.2 cm and good quality polished stainless steel strips (0.9 cm x 2.5 cm x 24 gauge). The stainless steel strips were polished using an emery cloth and a polishing paper # 320. The films deposited on glass substrates were used to study the properties of the films whereas that on the stainless steel were used for electrochemical PV-studies.

2.3.2 Cleaning the substrates

Substrate cleaning plays a vital role in deposition of the thin films. Following procedure was adopted for cleaning the substrates. The glass substrates were dipped into concentrated HNO$_3$ acid for 24 hours and washed with distilled water. The acid cleaned substrates were then washed with a detergent solution and distilled water and rinsed several times with the AR grade acetone and ethanol. All the substrates were kept under
double distilled water in an air tight compartment before use. The stainless steel substrates were first degreased with a detergent solution, polished using an emery cloth and washed several times with double distilled water and then with acetone.

2.3.3 Preparation of the solutions

All the chemicals used for deposition of the CoS and Co$_{1-x}$Zn$_x$S thin films were of the AR grade. The solutions were prepared in double distilled water. The different chemical precursors used were:

a) Cobalt sulfate, Sd-fine (India) Ltd.

b) Zinc Sulfate, Sd-fine (India) Ltd.

c) Thiourea, Sd-fine (India) Ltd.

d) Triethanolamine, Sd-fine (India) Ltd.

e) Ammonia (25% v/v) Sd-fine (India) Ltd.

2.3.4 Factors regulating chemical solution deposition

This is the most important part of the studies for the deposition of thin films. The growth of the films by this technique is found to be governed by various factors viz. bath composition, pH, deposition time and the deposition temperature [2, 3, 7, 9-13].

a) Bath composition

The growth rate and quality of the deposited films is found to be greatly influenced by the concentrations of the reacting species. The films deposited using low precursor concentrations are thin and non-uniform. This can be related to the insufficient supply of the ionic species at such concentration levels. On the other hand, when concentrations of
the species were increased, the quality and uniformity of the films went on increased and the films become thick enough. This is true up to a certain level of concentration and then saturation in film thickness was observed.

b) The pH

This is the most important factor in the chemistry of chemical solution deposition. Thus the desired films were obtained onto the substrate surface by optimizing the pH value of the solution bath.

c) Deposition temperature

The film growth rate is found to be temperature dependent. The rate of deposition increases with the bath temperature resulting into formation of the fine grained thin films. The deposition temperature was therefore varied to yield a good output product.

d) Deposition time

Thin film growth is time dependent. The film deposition time was therefore varied to get sufficient thickness on the substrate surface.

e) Speed of the mechanical churning

A constant but continuous mechanical churning of the reaction solution is essential to grow uniform, adherent and good quality films. The mechanical speed of churning the bulk of the solution was therefore optimized.

2.3.5 Synthesis of the CoS and Co$_{1-x}$Zn$_x$S thin films

The deposition of CoS and Co$_{1-x}$Zn$_x$S thin films was carried out under the same experimental conditions. The basic precursors used were cobalt sulphate and zinc
sulphate with appropriate quantities of triethanolamine (TEA) and an aqueous ammonia to adjust pH of the reaction solution and film layer adherence [7, 11, 14-16] respectively. CoS thin film optimization was done by varying TEA from 2ml to 6 ml and aqueous ammonia quantity was varied from 10 ml to 25 ml. Correspondingly, the reaction temperature parameter was optimized by the variation of temperature from 60°C - 90°C. And, speed of mechanical churning was varied from 45 rpm to 85 rpm. For concluding deposition of CoS and Co$_{1-x}$Zn$_x$S thin films, optimized parameters were selected. In actual, CoS deposition was carried by mixing 10 ml (1M) cobalt sulfate, 10 ml (1M) thiourea, 4 ml TEA and 15 ml (2.8M) ammonia solution. The total volume of the reaction mixture was then made to 200 ml by adding double distilled water. The beaker containing reactive solution was transferred to an oil bath at 353 K. The pH was found to be 9.0 ± 0.1. The glass substrates as well as stainless steel strips were kept vertically in a reaction mixture and rotated with a speed of 65 ± 2 rpm. After 90 min, the deposited substrates were taken out of the bath, rinsed with double distilled water, dried and kept in a dark desiccator. Similar procedure was adopted to synthesis Co$_{1-x}$Zn$_x$S (0.01≤ x ≤ 0.4) thin films. The solutions of cobalt sulfate and zinc sulfate were mixed in the required stoichiometric ratio (1-x): x: 1.

2.4 Measurements and Characterization of CoS and Co$_{1-x}$Zn$_x$S Thin Films

The properties of the thin films are a strong function of the preparatory technique used. Therefore, it is necessary to characterize the films before they from a part of the application. In this section, various characterization techniques are described in brief.
2.4.1. The film thickness measurement

The film thickness is the most important factor in thin film physics because most of the properties depend on the film thickness. There are various methods of determining the thickness of the film. Among various methods in practice, weight difference and interference technique are most suitable, convenient and requires no sophisticated instrumentation and process control.

a) Weight difference method

In these investigations the film layer thickness was measured by a weight difference - density method. The thickness of the film layer is related to its mass and area as;

\[ t = \frac{m}{A \cdot d} \] ...... (2.1)

where, \( d \) is the density of the material in gm/cm\(^3\)

b) Interference technique

The method is based on the accurate measurement of the fringe width of the interference pattern obtained on the film. A typical arrangement of an interferometer is shown in fig. 2.3. A sodium vapour lamp (\( \lambda = 5896 \) Å) was used as a monochromatic source of light.

The terminal layer thickness (\( t \)) and source wavelength (\( \lambda \)) are related as;

\[ t = \frac{\lambda \cdot d}{2x} \] ...... (2.2)

where, \( d \) is the length of the air film and \( x \) is the fringe width.

2.4.2. Wettability measurements

If a drop of liquid is placed on a horizontal solid surface in equilibrium with vapor phase, it spreads on the solid surface till the three interfacial forces balance each other.
Figure 2.3 An arrangement for terminal layer thickness measurement using interference technique.

These three forces act on a contact line due to interfacial tension. At equilibrium, the net force on a contact line must be zero. This is governed by Young’s equation [17];

\[ \gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \]  

(2.3)

where, \( \gamma_{sv} \), \( \gamma_{sl} \), \( \gamma_{lv} \) are the solid-vapour, solid-liquid and liquid-vapour interfacial energies, respectively and \( \theta \) is the contact angle. The contact angle (\( \theta \)) is the angle made by the tangent to the liquid-vapour interface drawn at the contact line that makes an angle (measured inside the liquid) with the solid surface, which is the characteristic of
the three-phase system (solid-liquid-vapor). The contact angle (θ) therefore, is a thermodynamic property [9, 17-19]. Fig. 2.4 shows three interfaces – solid-liquid, liquid-vapour, solid-vapour.

**Figure 2.4** A water droplet in equilibrium over a horizontal solid surface.

When γ_{sv} > γ_{sl}, then the liquid tends to flow over an exposed solid surface and θ is acute. This means that the surface is hydrophilic in nature. When γ_{sv} < γ_{sl}, then the liquid doesn’t stay on the solid surface and θ is obtuse means the surface is hydrophobic in nature. Hence, depending on the value of contact angle, the surfaces are classified as shown in fig. 2.4. The contact angle θ is directly measured using a contact angle meter (Rame-Hart, U.S.A.). A water drop was kept on the as-obtained CoS and Co_{1-x}Zn_{x}S thin film surfaces and the image of the drop was projected on the screen of the monitor with a CCD camera. This gives directly the value of θ after the proper adjustment of the
tangent to the water drop at the point of contact with the solid surface.

2.4.3 The chemical compositional analysis

a) An energy dispersive X-ray spectroscopy (EDS)

An EDS is an X-ray analysis technique used to identify the elemental composition of a specimen. EDS systems are the attachments to the SEM / FESEM and TEM instruments, where the imaging capability of the microscope is used to identify the specimen of interest. The data generated by an EDS consist of the spectra showing peaks corresponding to the elements making up the true composition of the specimen being analyzed. The technique can be a qualitative, or a semi-quantitative, or a quantitative and provides spatial distribution of elements through mapping [20-22].

In EDS, the specimen is bombarded with an electron beam inside the scanning electron microscope. The bombarding electrons collide with the specimen atoms knocking out some of them in the process. A position vacated by an ejected inner shell electron is eventually occupied by a higher-energy electron from an outer shell. To be able to do so, however, the transferring outer electron must give up some of its energy by emitting an X-ray. The amount of energy released by the transferring electron depends on which shell it is transferring from, as well as which shell it is transferring to. Furthermore, the atom of every element releases X-rays with unique amounts of energy during the transferring process. Thus, by measuring the amounts of energy present in the X-rays being released by a specimen during electron beam bombardment, the identity of the atom from which the X-ray was emitted can be established. The output of an EDS is an
EDS spectrum. The EDS spectrum is just a plot of how frequently an X-ray is received for each energy level. An EDS spectrum normally displays peaks corresponding to the energy levels for which the most X-rays have been received. Each of these peaks is unique to an atom and therefore corresponds to a single element. The higher the peak in a spectrum, the more concentrated the element is in the specimen. The elemental compositional analysis of the thin film samples was therefore carried out using a non-destructive energy dispersive spectroscopy (EDS) technique. The measurements were carried by an EDS tool attached to the FESEM unit (FESEM, Hitachi S-4700 Japan).

**b) The X-ray photoelectron spectroscopy (XPS)**

XPS was developed by K. Siegbahn in 1957 and is used to study the energy levels of atomic core electrons, primarily in solids [23-25]. Siegbahn referred to the technique as Electron Spectroscopy for Chemical Analysis (ESCA) and was awarded the Nobel Prize in 1981 for his contribution to the development of high-resolution electron spectroscopy [25]. Photoelectron spectroscopy is a surface characterization technique based on the photoelectric effect [25]. The absorption of a photon with a given energy $h\nu$ by the sample induces an electronic transition described by,

$$h\nu = E_f - E_i.$$  

(2.4)

where, $E_f$ and $E_i$ are the energies of the final and initial electronic states, respectively. After the absorption of the photon, the electron, which was originally occupied in a bound state of the discrete spectrum, is promoted either to the unoccupied part of the discrete spectrum or to the continuum of states above the vacuum level. The electrons
that are promoted above the vacuum level are characterized by their kinetic energy ($E_{\text{kin}}$), which is related to the binding energy of the initial state ($E_B$), to the energy of the incoming photon ($h\nu$) and to the work function ($\Phi$) of the electron analyzer by the following expression:

$$E_{\text{kin}} = h\nu - E_B - \Phi.$$  
(2.5)

In core level XPS, the intensity of those photoelectrons emitted by the sample (fig. 2.5) is measured as a function of their kinetic energies. Photoemission peaks are labelled according to the quantum numbers of the corresponding original levels, following the standard spectroscopic notations (orbital momentum $l = 0, 1, 2...$ denoted as s, p, d...). All the levels with $l \geq 1$ show the corresponding spin-orbit splitting appearing in the spectrum as a doublet with a characteristic energy separation.

A property of photoelectron which defines the surface sensitivity of the XPS method is the mean free path. Here the electron energy lies typically between 10 eV and 2000 eV and for these kinetic energies, the mean free path is approximately 0.5 nm - 3 nm, resulting in an extremely sensitive method for surface analysis.

The position of the peaks in an XPS spectrum that is recorded from a specific sample can be used to identify the constituent elements by comparison with the reference data available from the literature [20-25]. Quantitative analysis is also possible as the peak intensity is directly related to the concentration of atoms. Furthermore, the chemical environment of the elements present in the sample can be studied by means of XPS. The characteristic binding energies of the photoelectrons do not merely depend on the
specific element, but also on the chemical state of the corresponding atom. Chemical
shifts are recorded as a displacement (typically in the range of 0 to 3 eV) in binding
energies of photoelectrons excited from the atoms in a compound compared to the
energies of the corresponding pure substance. These binding energies increase with the
oxidation state of a substance, since part of the electronic density is transferred to the
oxidizing species, leaving the remaining electronic density unbalanced against the
positive nuclear charge. It is therefore possible to deconvolute a core level peak into its
different contributing parts for different oxidation states and/or partial changes of
electron density and the resulting peak areas can be related to the concentration of atoms
in the individual states [20-25].

Figure 2.5. Schematic representation of an XPS analysis.
Since, the escape depth of the photo-excited electrons is small (15-25 Å in case of XPS) it is important to perform these measurements on an extremely clean sample surface. Thus, all the measurements have to be carried out in an ultra-high vacuum (UHV) chamber (vacuum ~ 10^{-11} mbar). Fig. 2.5 represents schematic of the XPS analysis. XPS measurements were made on the CoS and Co_{1-x}Zn_xS thin film samples at room temperature with a SPECS PHOIBOS 150 hemispherical analyzer (SPECS GmbH, Berlin, Germany) in a base pressure of 1x10^{-10} mbar using monochromatic Al Kα radiation (1486.74 eV) as an excitation source.

2.4.4. The X-ray diffraction analysis (XRD)

An XRD technique is important method to identify non molecular and crystalline substances. It can be used to determine the crystal structure, unit cell parameters and content, including crystallite size. This structural data is useful in the explanation of trends in many properties. The X-rays are electromagnetic radiation of wavelength around 1Å. Diffraction arises from an interference between in phase adjacent scattering beams (Fig. 2.6).

![Figure 2.6. Schematic representation for derivation of Bragg’s law.](image)
When X-rays are scattered by two adjacent parallel planes of atoms or ions in the crystal separated by a perpendicular distance (d-spacing), the incident angle at which constructive interference occurs between beams of wavelength ($\lambda$) is given by the Bragg’s law,

$$2d \sin \theta = n\lambda. \quad \text{..... (2.6)}$$

A diffractometer measures the intensity of X-rays reflected from one stack of planes at a time, so it is of interest to examine what kind of spatial arrangements are best suited for such measurements. The intensity of a diffracted beam is measured by an electronic counter. This circuit counts the number of current pulses/sec and this number is directly proportional to the intensity of X-ray beam entering the counter or detector. A diffractometer is designed somewhat like a Debye Scherrer camera, except that a movable counter replaces the strip of film. In both the instruments, monochromatic radiation is always used and the X-ray detector (film or counter) is placed on the circumference of a circle centered on the powder specimen. The essential features of a diffractometer are shown schematically in the line diagram depicted in figure 2.7. A thin film specimen (C) is supported on a table (H) which can be rotated about an axis O perpendicular to the plane of the drawing. The X-ray source (S) is in line with focal spot on the target (T) of the X-ray tube; S is also normal to the plane of the drawing and therefore parallel to the diffractometer axis O. X-rays diverge from this source and are diffracted by the specimen to form a convergent diffracted beam which comes to a focus at the slit F and then enters the counter G. A and B are special slits which define and
collimate the incident and diffracted beams. The receiving slit and counter are supported on the carriage E which may be rotated about the axis O whose angular position $2\theta$ may be read on the graduated scale K. The supports E and H are mechanically coupled so that a rotation of the counter through $2\theta$ degrees is automatically accompanied by the rotation of the specimen through $\theta$ degree. This coupling ensures that the angle of incidence on, and reflection from, the specimen will always be equal to one another and equal to half the total of diffraction, an arrangement necessary to preserve focusing conditions. The counter may be power driven at a constant angular velocity about the diffractometer axis or moved by hand to any desired angular position.

The crystallographic aspects of the thin film samples were examined by an X-ray diffraction technique. A Bruker X-ray diffractometer (AXS-D8 Advance) with CuK\(\alpha\)
line ($\lambda = 1.54056$ Å) was used for this purpose. The range of 20 angles was from 20°-80°. The X-ray tube was operated at 40 kV, 30 mA with a scanning speed of 0.4 sec per step. The standard JCPDS data were used for the comparison. Analysis of the obtained diffractograms was done by accustomed JCPDS comparison method and X'Pert High Score Plus version 2.0 software.

2.4.5. The Fourier transform infrared (FTIR) spectroscopy

Fourier transform infrared spectroscopy (FTIR) is the most powerful tool for identifying types of the chemical bonds (functional groups) [20]. FTIR is an indispensable tool in the detection of the presence of capping agents, their interaction with the formed nanoparticles and so on. The wavelength of light absorbed is characteristic of the chemical bond as can be seen in the annotated spectrum. By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined. Molecular bonds vibrate at various frequencies depending on the elements and the type of bonds. For any given bond, there are several specific frequencies at which it can vibrate. These oscillatory motions are a complex function of the infinite series of the terms and are explained mathematically using sine and/or cosine functions. This representation is called Fourier series.

FTIR instruments employ interferometer technique for the collection of spectral information and the spectra are calculated as an inverse Fourier transform of the interferogram. The block diagram of a typical FTIR spectrometer is shown in fig. 2.8. All samples for the FTIR measurements were taken directly from thin films and scanned
Figure 2.8. Block diagram of a typical FTIR spectrometer.
2.4.6 The electron microscopies

a) Scanning electron microscopy (SEM)

A scanning electron microscope (SEM) based on the secondary emission of the electrons was developed at the RCA Laboratories in New Jersey under war time conditions [21, 22]. Further, SEM development occurred after the II World War, when Charles Oatley and colleagues began a research and construction program in the Engineering Department at Cambridge University. Their first SEM images were obtained in 1951 and a commercial model (built by the AEI Company) was delivered to the Pulp and Paper Research Institute of Canada in 1958. Sustained commercial production was initiated by the Cambridge Instruments Company in 1965. A modern SEM provides an image resolution typically between 1 nm and 10 nm, much superior to the light microscopes. In addition, SEM images have a relatively large depth of focus. A SEM bombards a specimen with a sharply focused beam of electrons and detects the resulting electrons that scatter out of the specimen. A SEM uses magnetic lenses to focus the electron beam. Unlike the lenses in an optical microscope, the magnetic lenses serve to demagnify (i.e. make smaller) the image of the electron gun rather than to magnify the image of the specimen. Initially, the electron beam is of the order of tens of microns. The beam is focused to a very small spot of the order of several nanometers in diameter through a demagnification of about 1/5000 so that it can sample the specimen surface as finely as possible. Electromagnetic deflection coils raster this spot over the surface to create an image just like the beam in a cathode ray tube (CRT) is scanned.
over a phosphor-coated screen. In a CRT, a flat surface hit by the electrons displays an image; in a SEM the response of the surface hit by the electrons is measured and displayed as an image. The signal produced by electrons scattered out of the specimen is displayed on a CRT screen or acquired by a digital frame grabber that is scanned in synchrony with the scanning of the SEM beam over the surface. Fig. 2.9 represents the schematic block diagram for a SEM setup.

The surface morphology of the semiconductor material plays a vital role in the understanding of device performance; therefore it was essential to examine the surface analysis. A scanning electron microscope, (SEM: JEOL 6360-2300), was used to observe the surface topography of the films. The accelerating voltage was kept at 20 kV.

b) Field emission scanning electron microscopy (FESEM)
The field emission scanning electron microscope (FESEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the shells in atoms that make up the sample producing signals that contain information about the sample’s surface topography and composition. The spot size in a Field Emission SEM is smaller than in conventional SEM and can therefore produce very high-resolution images revealing details in the range of 1 to 5 nm in size. Fig. 2.10 represents the schematic block diagram for FESEM setup. FESEM micrograph images were taken on a Hitachi S-4700, FESEM with a Schottky electron gun. Measurements were carried out at an accelerating voltage range of 5 kV - 15 kV.

**Figure. 2.10.** Schematic representation of FESEM setup.
c) Atomic force microscopy (AFM)

A scanning tunneling microscope was developed at the IBM Zurich Laboratory by Binnig (1982) and earned the Nobel Prize in Physics (1986 shared with Ernst Ruska). It quickly inspired about other types of scanning-probe microscopes, such as the atomic force microscope (AFM), in which a sharp tip (at the end of a cantilever) is brought sufficiently close to the surface of a specimen so that it essentially touches it and senses an interatomic force. For many years, this principle had been applied to measure the roughness of the surfaces or the height of the surface steps with height resolution of a few nanometers. In the 1990’s, the instrument was refined to give near-atomic resolution [20-22].

The atomic force microscopy (AFM) probes the surface of a sample with a sharp tip, a couple of microns long and often less than 100 Å in diameter. The tip is located at the free end of a cantilever, which is 100 to 200 μm long. The forces between the tip and the sample surface cause the cantilever to bend or deflect. A detector measures the cantilever deflection as tip is scanned over the sample surface or the sample is scanned under the tip. The measured cantilever deflection allows a computer to generate a map or surface topography. Several forces contribute to the deflection of an AFM cantilever. AFM operates by measuring the attractive or repulsive forces between a tip and the sample. The mechanical force is repulsive if the tip is in direct contact with the sample, but at a small distance above, the tip senses an attractive force (van der Waals). Alternately, a 4-quadrant photodetector can sense torsional motion (twisting) of the
AFM cantilever, which results from a sideways frictional force giving an image that is essentially a map of the local coefficient of friction. Additionally, with a modified tip, the magnetic field of a sample can be monitored, allowing the direct imaging of surface topography in terms of magnetic mapping (MFM).

Surface topographies of the as-obtained CoS and Co1-xZnxS thin films were therefore analyzed by an atomic force microscope using an AFM-Innova from Bruker instruments in non-contact tapping mode. The measurements were performed in air at room temperature (25°C, RH=35%). AFM topographic images of 3 µm x 3 µm and 10 µm x 10µm scan area were obtained. The SPIP software (Image Metrology A/S) was used for the image processing. The schematic representation of an AFM measurement technique is shown in fig. 2.11.

Figure 2.11. Schematic representation of AFM measurement technique.
d) Magnetic force microscopy (MFM)

Magnetic force microscopy (MFM) has found a widespread application in magnetic recording research, mainly because it is a relatively cheap and high resolution imaging technique that does not require sample preparation. Magnetic force microscopy is a secondary imaging mode derived from tapping mode that maps the magnetic force gradient above the sample surface.

This is performed through a patented two-pass technique (Lift mode) [7, 11]. Lift mode separately measures topography and another selected properties (magnetic force, electric force, etc.) using the topographical information to track the probe tip at a constant height (Lift Height) above the sample surface during the second pass. In an MFM, the magnetic stray field above a very flat specimen or sample is detected by mounting a small magnetic element, the tip, on a cantilever spring very close to the surface of the sample. The force on the magnetic tip is detected by means of a cantilever and a displacement sensor. The positioning system brings the sample close to the tip (coarse positioning) and scans the tip over the sample area to obtain an image (fine positioning). The MFM measurement technique is shown in fig. 2.12.

Magnetic mapping topography of our samples was done by using an AFM instrument (Innova: Bruker) with low coercivity probe (MESP-LC). The measurements were performed using dynamic/ magnetic force microscopy (MFM) mode (lift mode height: 40nm) in air at room temperature (25°C, RH=35%). Since it is 2nd pass technique, MFM
topographic images of same 3 µm x 3 µm and 10 µm x 10µm scan area were obtained. The SPIP software (Image Metrology, A/S) was used for the image processing.

![Figure 2.12. Graphic representation of MFM measurement technique.](image)

**Figure 2.12.** Graphic representation of MFM measurement technique.

### 2.4.7. Optical measurements

Ultraviolet and visible (UV-Vis) absorption spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. Absorption measurements can be at a single wavelength or over an extended spectral range. Ultraviolet and visible light are energetic enough to promote outer electrons to higher energy levels and UV-Vis spectroscopy is usually applied to molecules or inorganic complexes in solution. The UV-Vis spectra have broad features.
that are of limited use for sample identification but are very useful for quantitative
determinations. The concentration of an analyte in solution can be determined by
measuring the absorbance at some wavelength and applying the Beer-Lambert Law [26-
28]:
\[ A = -\log_{10}\left(\frac{I}{I_0}\right) = \varepsilon C L \] 
\[ \ldots \quad (2.7) \]
where, A is the measured absorbance, I₀ is the intensity of the incident light at a given
wavelength, I is the transmitted intensity, L is the path length through the sample and c
is the concentration of the absorbing species. For each of the species and wavelengths, \( \varepsilon \)
is a constant known as the molar absorptivity or extinction coefficient. Since the UV-Vis
range spans the range of human visual acuity of approximately 400 - 780 nm, UV-Vis
spectroscopy is useful to characterize the absorption, transmission and reflectivity of a
variety of technologically important materials, such as pigments, coatings, windows and
filters. This more qualitative application usually requires recording at least a portion of
the UV-Vis spectrum for characterization of the optical or electronic properties of the
materials. Single beam spectrophotometers are often sufficient for making quantitative
absorption measurements in the UV-Vis spectral region. The typical optical absorption
measurements were made in the wavelength range from 200 nm to 1600 nm by using a
BIO-AGE UV-VIS 2800 PC, UV-VIS spectrophotometer at room temperature. A
substrate absorption correction was made by placing an identical, uncoated glass
substrate in the reference beam. The optical transmission was measured as a function of
the wavelength (\(\lambda\)). The spectra were mainly used to determine the absorption coefficient (\(\alpha\)), energy band gap (\(E_g\)) and the type of optical transitions.

2.4.8. The electrical transport measurements

The electrical transport properties are of great importance in deciding quality of the semiconductor device. It involves measurements on the electrical conductivity and thermoelectric power. The nature of the conduction mechanism, activation energy of an electrical conduction, carrier density, mobility, barrier height etc were determined from these observations.

a) The electrical conductivity measurements

The electrical conductivities of all the thin films were measured using a dc two-probe method [28-30]. The schematic setup for electrical conductivity measurements is as shown in fig. 2.13. It consists of two brass plates of the size 10 cm \(\times\) 5 cm \(\times\) 0.6 cm, one

![Schematic arrangement for the measurement of an electrical conductivity.](image)

**Figure 2.13.** Schematic arrangement for the measurement of an electrical conductivity.
of the plates is fixed tightly on the asbestos base of dimension 25 cm × 25 cm. Two strip heaters (65 W) were kept in parallel on the first brass plate and other plate was fixed tightly to the lower plate i.e. strip heaters were sandwiched between the two brass plates to achieve the uniform temperature. A pair of the sample holder whose dimensions are 3 cm × 0.5 cm × 0.6 cm was designed and fixed exactly at the center of the upper plate. A mica sheet was used to insulate brass plates and the films. A cover was put on the assembly to prevent the thermal loss. A quick drying silver paste was applied at the ends of the film for ohmic contact purpose. A regulated dc power supply was used to pass the current through the sample. A constant voltage of 25 V was applied across the sample. A digital multimeter (HIL-2665 4½) was used to measure the potential drop across the sample and a current flowing through the circuit was measured by a sensitive DNM-121 4½ digit nano-ammeter. A calibrated chromel - alumel thermocouple of 24-gauge size was used to sense the working temperature.

b) Thermoelectric power measurements

If some metal contacts are applied to the two ends of a semiconductor and if one junction is maintained at higher temperature than the other, a potential difference is developed between the two electrodes. This thermoelectric or Seebeck voltage is produced partly because: (i) the majority carriers in the semiconductor diffuse from hot to cold junction, thus giving a potential difference between the ends of a specimen. This voltage builds up to a value such that the return current just balances the diffusion current when a steady state is reached, (ii) other part which contributes to the
thermoelectric voltage is the contact potential difference between metal and semiconductor, which occurs at the two junctions. In the semiconductor, if the charge carriers are predominantly electrons, the cold junction becomes negatively charged and if the charge carriers are positive holes, the cold junction becomes positively charged. The magnitude of the developed voltage is proportional to the difference in temperature between the hot and cold junctions, if the temperature difference is small. From the sign of the developed thermoelectric voltage, it is thus possible to deduce whether a given specimen exhibits n-or p-type conductivity. The thermoelectric power (TEP), which is defined as the ratio of thermally generated voltage to the temperature difference across the semiconductor, gives the information about the type of carriers in the semiconductor. The thermoelectric power (TEP) measurements were therefore carried out for all the samples using an indigenous setup developed in our laboratory [2, 3, 9]. Fig. 2.14 shows

**Figure 2.14.** Schematic arrangement for the measurement of thermopower.
a schematic diagram of a TEP measurement set up. It consists of two copper blocks of the dimensions 5 cm × 4 cm × 1.2 cm fitted on an asbestos sheet supported by the bakelite sheet. The plates were arranged in parallel with a distance of approximately 3 cm apart. The plates were pitched to a size of mini heaters from the bottom and the mini heaters of the different wattage (65W and 35W) were fixed in them. Care was taken of the electrical insulation between the mini heaters and copper blocks by means of the mica sheets. A Cr-Al thermocouple was fitted at the center of the block. The sample holder was fixed on the top adjacent nearer edges of copper blocks lengthwise. The sample used in this study was 3 cm × 0.5 cm. The dimensions of the substrate holder were 3 cm × 0.5 cm × 0.5 cm. The sample was electrically insulated from the copper blocks and the substrate holder by means of the mica pieces. Copper strips were used for press contacts purpose. A quick drying silver paste was used for ohmic contacts purpose. The Bakelite box is covered to prevent any thermal loss. Thermo-voltage was measured by a high sensitivity Hewlett-Packard 6½ digit multimeter and gradient of temperature was measured by a milli-voltmeter sensed by a Cr-Al thermocouple.

c) Photosensitivity measurements

Photo-excited electron produces an electronic conduction in the solids. When photon energy is greater than the band gap of the material, excitation takes place. The interaction of a solid with a light of appropriate wavelength creates electron-hole pairs. The phenomenon of photo-conductivity is therefore, the increase in electrical conductivity of a solid when irradiated with light. The concentration of carriers in
illuminated materials is in excess of their values in the dark. The excited carriers decay back to their equilibrium values when the light is switched off.

Recombination is the process wherein the decay occurs. This may be radiative, in which an electron occupying a higher energy state makes transition to an empty lower energy state accompanied by the emission of light. Many semiconductors exhibit photoconductivity and the phenomenon is the basis of many optoelectronic applications.

The sensitivity of the material can be measured by determining the electrical conductivity in dark and in light. At a fixed temperature of the film, the d. c electrical conductivity in light was measured by the same two probe conductivity measuring unit. For this purpose, the light was allowed to incident with constant illumination on the sample from a fixed distance. The resulting photocurrent under illumination was measured for the representative composite films [2, 3, 28-30]. The photo-sensitivities of the samples of various compositions were then calculated using:

\[ s = \frac{\sigma_L - \sigma_d}{\sigma_d} \]  \( \ldots (2.8) \)

where, \( \sigma_L \) is the electrical conductivity in light and \( \sigma_d \) is the electrical conductivity in dark.

2.5 The Measurements on Electrochemical Photovoltaic (PV) Cells

2.5.1 Electrical contacts

The nature of the electrical contacts between a photoelectrode material and a substrate was tested for both types of polarities. A better ohmic contact is required for a better device performance. In the present investigation, all the films were deposited on
stainless steel strips. The nature of the contact was then determined from current-voltage (I-V) measurements across the contact. A dc regulated power supply was used to provide voltage across the contact and the current through the contact was measured with a Hewlett-Packard 6½ digit multimeter.

2.5.2. Design and fabrication of a PV-cell

A schematic diagram of an electrochemical PV cell fabricated in our laboratory and used in these investigations is shown in fig. 2.15 [28-30]. It consists of two test tubes: one hard glass test tube of inner diameter 2.7 cm and length 7 cm and other an ordinary test tube of inner diameter 1.5 cm and length 12 cm. The two test tubes were coupled by a small capillary of 0.3 cm. This H-shaped assembly was fitted in a copper vessel of suitable size. A window of the dimension 2 cm × 0.5 cm was made for illumination of the electrode material. A PV cell of the configuration CoS/Co_{1-x}Zn_{x}S/electrolyte/C was then devised with a graphite rod sensitized in a medium concentrated CoS solution for about 24 hours. The distance between the photoelectrode and the counter electrode was about 0.3 cm. A rubber cork was used to air tighten the cell and support both the counter electrode and photoelectrode. The active area of the sample exposed to light was defined by a common epoxy resin.

a) Choice of an electrolyte

The match of an electrolyte redox couple was tackled through the various electrolyte studies. Sulphide/Polysulfide, Hydroquinone, KCl, NH_{4}Cl, DMSO, Iodite/Polyiodite
and H₂SO₄ electrolytes were prepared in double distilled water and immediately used for the studies. Based on these studies KCl electrolyte has been used.

2.5.3. The electrical properties of a PV-cell

The electrical properties of a cell coupled with nature of the junction formed and the charge transfer process across the electrode/electrolyte interface were examined. These properties were studied through the I-V and C-V characteristics in dark, barrier height measurements and power output curves in light.

![Schematic diagram of an electrochemical PV cell](image)

**Figure 2.15.** A schematic diagram of an electrochemical PV cell.

a) Current-voltage characteristics in dark

For I-V characteristics, a conventional 2-electrode cell geometry as constructed was used. The applied voltage to the junction was varied with a helical potentiometer (10
turn, 1KΩ) and was recorded by an Agronic-113 4½ digit voltmeter. The current flowing through the junction was measured by a Hewlett- Packard 6 ½ digit multimeter.

b) Capacitance-voltage characteristics in dark

The C-V measurements under reverse bias condition were carried out using 3-electrode cell geometry, viz. a photoelectrode, a counter electrode and a saturated calomel electrode (SCE) as a reference. The potential applied across the junction V (vs. SCE) was varied by a 10 turn, 1 KΩ helical potentiometer and was recorded by an Agronic-113 4½ digit voltmeter. The junction capacitance was measured by an Aplab - 4910 4½ digit capacitance meter at a superimposed frequency of 1 KHz, 1 Vpp ac.

c) The barrier height measurements

The barrier heights at the various electrode/ electrolyte interfaces were determined by measuring the temperature dependence reverse saturation current of the various cells. The reverse saturation current was recorded at various temperatures from 90°C down to the room temperature.

d) The power output characteristics

The power output curves were obtained for all the cells under a steady state illumination intensity of 50 mW/cm². A 200 W tungsten filament lamp was employed to illuminate the cells. A water filter was interposed between a lamp and a cell to avoid heating of the cell. The illumination intensity was measured using a LX-101 (Lutron, Taiwan) lux-meter.

2.5.4. The optical properties of a PV- cell
a) Spectral response

The spectral response studies on these cells were conducted. The range of wavelengths used was from 350 nm to 1250 nm. The short circuit current was recorded with a Hewlett-Packard 6½ digit multimeter.

b) Photo response

The photo responses of all the cell structures were recorded by measuring the short circuit currents ($I_{sc}$) and open circuit voltages ($V_{oc}$) at different illumination intensities (5 mW/cm$^2$ - 50 mW/cm$^2$). The illumination intensity was measured with a LX-101 (Lutron, Taiwan) lux-meter, whereas the open circuit voltages and short circuit currents were measured as usual.

c) Transient response

This is time dependent performance of the various cells and involves measurement of either a short circuit current ($I_{sc}$) or an open circuit voltage ($V_{oc}$) as a function of the rise or decay times. The $I_{sc}$ and $V_{oc}$ were measured in the same fashion as above.
References


    (b) S.T. Mane, Ph.D. Thesis (2012), Solapur University, Solapur (M.S.) India.


