Chapter 3

Bi$_2$S$_3$: Synthesis, Characterization and Its Application as a Sensitizer In Semiconductor Sensitized Solar Cells

This Chapter describes methods and techniques applied for synthesis of Bi$_2$S$_3$ nanoparticles, sensitization of previously prepared porous photoanode of SnO$_2$ with Bi$_2$S$_3$ and cell fabrication using SnO$_2$/Bi$_2$S$_3$ photoanodes. The first part deals with introduction, synthesis of Bi$_2$S$_3$ and supporting experiments for device fabrication. The second part of the chapter describes the techniques used for characterization of the synthesized materials. The third part describes results obtained and discussion over effect of sensitization time on properties of Bi$_2$S$_3$ and Bi$_2$S$_3$ sensitized porous SnO$_2$ photoanodes and their performance in SSSC.
<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Index</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Chapter 2: Experimental Methods: Synthesis and Characterization of Materials</td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>Introduction: Thin Film Technology</td>
<td>41</td>
</tr>
<tr>
<td>2.2</td>
<td>Chemical bath deposition: Method employed in present work</td>
<td>43</td>
</tr>
<tr>
<td>2.2.1</td>
<td>Concept of supersaturation, solubility product and ionic product</td>
<td>44</td>
</tr>
<tr>
<td>2.2.2</td>
<td>Effect of Preparative Parameters</td>
<td>47</td>
</tr>
<tr>
<td>2.2.2.a</td>
<td>Substrate</td>
<td>47</td>
</tr>
<tr>
<td>2.2.2.b</td>
<td>pH</td>
<td>47</td>
</tr>
<tr>
<td>2.2.2.c</td>
<td>Complexing agent</td>
<td>47</td>
</tr>
<tr>
<td>2.2.2.d</td>
<td>Temperature</td>
<td>48</td>
</tr>
<tr>
<td>2.2.2.e</td>
<td>Doping</td>
<td>48</td>
</tr>
<tr>
<td>2.3</td>
<td>Introduction: Characterization Techniques for Thin Films</td>
<td>49</td>
</tr>
<tr>
<td>2.3.1</td>
<td>X ray diffractometry</td>
<td>49</td>
</tr>
<tr>
<td>2.3.2</td>
<td>Scanning electron microscopy</td>
<td>52</td>
</tr>
<tr>
<td>2.3.3</td>
<td>Energy dispersive X ray spectroscopy</td>
<td>55</td>
</tr>
<tr>
<td>2.3.4</td>
<td>UV-Visible spectroscopy: An optical absorption</td>
<td>55</td>
</tr>
<tr>
<td>2.3.5</td>
<td>Photoluminescence measurement</td>
<td>57</td>
</tr>
<tr>
<td>2.3.6</td>
<td>Contact angle measurement</td>
<td>59</td>
</tr>
<tr>
<td>2.4</td>
<td>Solar spectrum, irradiation and Solar cell characteristics</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>References</td>
<td>64</td>
</tr>
</tbody>
</table>
2.1. Introduction: Thin Film Technology

Thin film is a layer or deposition of materials such as metals, semiconductors and ceramics, having thickness ranging from few nanometers to several micrometers. Thin film is a young and emerging field in science and technology. This is convergence of materials science, surface science and applied physics and has become an identifiable integrated discipline of science. Nowadays, studies on the thin film deposition is being pursued with increasing interest on account of its potential applications in range of semiconductor based optoelectronics devices including photovoltaics [1]. The physical properties of semiconductors in particular structural, optical and electrical ones can be tailored by controlling the crystal size of material. Optimization of these properties of semiconductor chalcogenides is of particular interest in view of different areas of applications. Preparation techniques of producing the films of semiconductor chalcogenides range from very simple, cheap to complex and very expensive ones depending on the substrate to be coated with materials and required area of applications [2]. The methods for depositing thin films possibly will be broadly classified under two titles: physical and chemical techniques. The physical methods include the broad categories of sputtering, physical vapour deposition (PVD) and plasma techniques etc. On the other hand, chemical techniques include chemical vapour deposition (CVD), spray pyrolysis, electrochemical deposition (ECD), anodization, spin coating, dip coating and chemical bath deposition (CBD) etc. The different deposition techniques are tabulated in Table 2.1.

In the present study, being cost effective and facile technique, CBD is used for the deposition of films. For the sake of understanding the basic principle involved in the CBD, theoretical background is given in section 1. Thin films prepared by using CBD will be further characterized by means of structural, surface morphological, optical and contact angle measurements. It is therefore necessary to study the basis involved in the characterization techniques of the material in order to assess the scope for further improvement in utility and efficiency. Section 2 highlights on various characterization techniques such as X-ray diffractometry (XRD), scanning electron microscopy (SEM), UV-Vis spectroscopy, contact angle measurement (CAM) and photoluminescence (PL) used for the study of the physicochemical properties of thin films. Photovoltaic performance of the devices fabricated using these materials as sensitizers in semiconductor sensitized solar cells (SSSC) was evaluated with the help of current density (J) versus photovoltage (V) curves. In order to understand some of
the basic aspects of photovoltaic parameters measurements in SSSC, Section 3 highlights the theoretical background of measurement of cell parameters.

Table 2.1 Different deposition techniques for obtaining thin and thick films

<table>
<thead>
<tr>
<th>Thin and Thick Film Deposition Techniques</th>
<th>Physical Deposition</th>
<th>Chemical Deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sputtering</td>
<td>Evaporation</td>
<td>Gas phase</td>
</tr>
<tr>
<td>Glow discharge</td>
<td>Vacuum</td>
<td>CVD</td>
</tr>
<tr>
<td>DC</td>
<td>Resistive heating</td>
<td>Laser CVD</td>
</tr>
<tr>
<td>Triode</td>
<td>Flash</td>
<td>Photo CVD</td>
</tr>
<tr>
<td>Getter</td>
<td>Electron beam</td>
<td>Plasma CVD</td>
</tr>
<tr>
<td>Radio frequency</td>
<td>Arc</td>
<td>Metal-Organo CVD</td>
</tr>
<tr>
<td>Magnetron</td>
<td>Laser</td>
<td>ECR-Plasma CVD</td>
</tr>
<tr>
<td>Ion beam</td>
<td>RF heating</td>
<td></td>
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<tr>
<td>AC</td>
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<td></td>
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</tbody>
</table>
Section 1

This section deals with the basic concepts such as ionic product, solubility product, formation of thin films and precipitate in the solution in CBD.

2.2 Chemical bath deposition: Method employed in present work

For the synthesis of bismuth and antimony chalcogenides and sensitization of previously prepared tin oxide photoanodes in the present work, chemical bath deposition (CBD) which is also known as solution growth, controlled precipitation, or simply chemical deposition, is used. It is an analogue, in the liquid phase, of the well-known chemical vapour deposition in the gaseous phase. The reaction takes place between the dissolved precursors generally in aqueous solution at low temperature. Since last few decades it is attracting researchers due to following advantages:

1. It does not require sophisticated instrumentation like vacuum system or expensive equipments.
2. Simple equipments like hot plate with magnetic stirrer are sufficient for deposition.
3. The starting materials are cheap and easily available.
4. A large number of substrates can be coated in a single set of reaction with proper arrangement.
5. Low temperature deposition is possible, which allows use of low melting point substrates and low boiling point media i.e. aqueous solutions. This also avoids oxidation and corrosion of metallic surfaces during deposition.
6. The stoichiometry of the product can be achieved by owing to the solubility product which also helps to produce homogeneous phase.
7. Large surface area, well adhered and thin films can be obtained since the basic building blocks are the ions instead of atoms.
8. The preparative parameters are easily controllable therefore, better structure can be obtained.
9. Doping agents can easily be added.
10. Low cost, reproducible and easy method of deposition.

CBD is fundamentally a simple, facile and effective technique for deposition of a wide variety of inorganic compound films from liquid (usually aqueous) solutions. The deposition is carried out in aqueous (acidic as well as alkaline) solutions. The deposition is mainly based on the degree of supersaturation of solution
and nucleation on the surface of the substrate i.e. on reaction rate. These processes are the function of some preparative parameters like concentration, deposition time, pH, and temperature. Optimization of these parameters in order to get uniformly deposited thin films is the focus argument of CBD technique.

### 2.2.1 Concept of supersaturation, solubility product and ionic product:

Sparingly soluble salt AB, when placed in solvent, a saturated solution containing A\(^+\) and B\(^-\) ions in contact with undissolved solid AB is obtained and equilibrium is established between the solid phase and ions in the solution, written as below,

\[
AB (S) = A^+ + B^- \tag{2.1}
\]

Applying law of mass action to this equilibrium,

\[
K = \frac{[A^+ B^-]}{[AB]} \tag{2.2}
\]

Where, \([A^+], [B^-]\) and \([AB]\) are concentrations of \(A^+, B^-\) and \(AB\) in the solution respectively.

The concentration of a pure solid phase is a constant number i.e. \(AB (S) = \text{constant}\)

\[
\star AB (S) = K' \tag{2.3}
\]

\[
\star K = \frac{[A^+ B^-]}{K'} \text{ or } K K' = [A^+ B^-] \tag{2.4}
\]

Since \(K\) and \(K'\) are constant, the product \(K K'\) is also constant, say \(K_s\), therefore equation (2.4) becomes,

\[
K_s = [A^+ B^-] \tag{2.5}
\]

\(K_s\) is called “solubility product” and gives the numerical relationship which originates among the concentrations of ions in reaction, when saturated solution is in contact with its own solid phase. However, \([A^+ B^-]\) is called as the “ionic product” (\(K_i\)). When the solution is saturated, the \(K_i\) is become equal to the \(K_s\). But, when \(K_i\) exceeds the \(K_s\) i.e. \(K_i/ K_s = S > 1\), the solution is supersaturated, precipitation occurs and ions combine on the substrate and in the solution to form nuclei. Nucleus is the minimum number of ions or molecule required to produce second stable phase in contact with solution. The process of formation of nucleation in the solution is important for obtaining precipitation. Temperature, reaction conditions, concentration of reagent, and solubility of the precipitate including particle size are the factors which decide the supersaturation of the system.

Therefore, to achieve a controlled precipitation one can add complexing agent
(X) to obtain a stable complex (AX) with metallic ion (A) that controls its concentration.

\[
\text{nA + pXA_n + X_p} \quad (2.6)
\]

The rate at which nuclei form in a solution, is dependent on the degree of supersaturation. The rate of nucleation which decides the growth and quality of film deposition increases exponentially in higher supersaturated solution. Rate of nucleation = \( K_o [Q-S] X \), provided \( X > 1 \), Where \( Q \) is concentration of solute in solution, \( K_o \) and \( X \) are constants. The subsequent step to nucleation is the beginning of the growth of the particles with nuclei or other seed particles present in solution. In this case of ionic solid, the process involves deposition of cations and anions on appropriate sites \[15\] as shown in following equation.

\[
(\text{AB})_n + \text{A}^+ + \text{B}^- \rightarrow (\text{AB})_{n+1} \quad (2.9)
\]

\[
(\text{AB})_{n+1} + \text{A}^+ + \text{B}^- \rightarrow (\text{AB})_{n+2} \quad (2.10)
\]

where ‘\( n \)’ is the minimum number of \( \text{A}^+ \) and \( \text{B}^- \) required for giving stable phase \( (\text{AB})_n \). The rate of growth is directly proportional to the supersaturation i.e. Rate of growth = \( K_o' a (Q-S) \), where ‘\( a \)’ is the surface area of the exposed solid and \( K_o' \) is the constant, which is a characteristic of the particular precipitate. If the supersaturation is maintained at low level throughout, then precipitation occurs which may led to nucleation. As a result of this, great number of centers will be available in solution upon which, growth process can take place where none of the particles grow very large and a colloidal suspension is formed. Under some circumstances, so formed colloidal particles can come together and adhere to one another and the resulting solid is called colloidal precipitate and process by which it is formed is called ‘coagulation’ or ‘agglomeration’. The size of so formed crystals is dependent on the mechanism followed during the growth of crystallites. The growth mechanism of thin film deposition process can be broadly classified into two types.

i) ‘Ion-by-ion growth’ where deposition process involves the ion-by-ion deposition at nucleation sites on the immersed surfaces. During this process, nucleation is slower and growth takes place at a solid surface not in the bulk of solution. This led to two dimensional depositions, which in contrast with the bulk formation in cluster mechanism. The further growth of crystallite may terminate when it comes in contact with another adjacent crystal or surface active species. Besides, the balance between
surface and bulk energies is also a valid reason for deciding critical nuclei of crystallite in ion-by-ion mechanism. However, presence of substrate may also stabilize the nucleus which is unstable in isolated state in solution by providing support to it. Many researchers have reported ion-by-ion growth for PbSe, CdS, PbS and HgS thin films [16, 17].

ii) In cluster mechanism, nucleation takes place by adsorption of the colloidal particles and growth takes place as a result of surface coagulation of these particles, giving thin and adherent film [18]. During this kind of deposition the crystal size of final product is found to be a function of temperature of reaction bath.

The kinetics of the growth depends on various deposition parameters and the number of preparative parameters and the methods of preparation [17]. The conclusion is ion-by-ion growth results in thin, hard, adherent and specularly reflecting films whereas cluster-by-cluster growth gives thick powdery and diffusely reflecting films. In both these mechanisms once nucleation occurs, the deposition rate rises rapidly until the rate of deposition becomes equal to zero i.e. $IP = SP$ or $S = 1$. Consequently, film attains a terminal thickness which is maximum attainable thickness (under given set of experimental conditions) therefore, it is called as ‘terminal thickness’.

The experimental set-up employed for the growth of the films from bulk precipitation of the solution, is shown in Figure 2.1. Water or paraffin bath with constant stirring is used to heat the chemical bath at a desired temperature.

![Figure 2.1 Experimental set-up of chemical bath deposition [17].](image-url)
2.2.2 Effect of Preparative Parameters

The number of nucleation centers available in the reaction bath, supersaturation of the solution, which is defined by ratio of $K_I / K_S$ and rate of stirring are the key parameters which decide the rate of deposition and thickness of final film in CBD. The growth kinetics depends on the concentration of ions, their velocities and nucleation-growth processes on immersed substrates. The deposition rate and thickness of film can be controlled by varying the optimizing parameters like pH, temperature, and concentration of precursor ions, complexing agent, and the substrate [3-8]. The effect of various deposition parameters on kinetics and deposition of films in CBD are discussed below:

a) Substrate

The feasibility of use of any substrate (need not to be transparent and electrically conducting) is one of the advantages of CBD, provided the substrate is chemically inert. Glass is very commonly used substrate in CBD for deposition. However, in spite of inertness of substrate, the surface of glass is reactive due to the presence of surface hydroxyl group. Many plastics can also be coated using CBD. As discussed earlier the presence of the substrate in the solution may provide the stability to the unstable ion i.e. may affect the surface energy of growing nucleus and thus can modify its critical radius having ending effect on crystallite size of final product. Therefore, use of different substrates or surface treatment to the substrate can vary the properties of final product.

b) pH

The reaction rate as well as rate of deposition depends on the supersaturation condition: lower the supersaturation, the slower the formation of AB (where A and B is the number of metals and chalcogenides ions respectively). If the concentration of OH$^-$ ion in the solution is higher, the A ion concentration will lower and therefore, reaction rate will be slow. Hence, to control the concentration of A ion which helps to get uniform films, it is important to optimize the pH of the solution.

c) Complexing agent

In chemical solution technique, to avoid bulk precipitation of materials, complexing agents usually of intermediate strength are added to metallic ions. This helps to form stable complex of agent with metallic ions that controls concentration of A ions during reaction. Increase in the concentration of complexing agent leds to decrease in the concentration of metal ions, which causes decrease in the reaction &
deposition rate, hence, affects quality of films. As the precursors of chalcogenides are not stable, optimization of concentration of complexing agent is necessary in order to get uniform and visible depositions.

d) Temperature

The effect of temperature on crystal size during synthesis is instinctively recognized. In addition, the dissociation of complex and the anion of the compound depend on the temperature. At the higher temperatures, the dissociation is greater and gives higher concentrations of ions that result in higher rates of deposition. Higher temperatures mean faster and inter nucleation between separate nuclei, leading to larger crystals. However, since CBD is a solution technique, which always occurs from aqueous solutions in limited temperature range, therefore it has another effect of temperature during synthesis which may also be more important in order to control the reaction rate. This is the balance between thermodynamic stability and kinetics of very small nuclei in an aqueous phase, which are thermodynamically unstable in solution. The limit of thermodynamic stability which decides the critical radius of nuclei, ‘R’, is determined by the balance between surface and bulk energies of the growing nucleus. This balance depends not only on the material itself but very importantly also on the surrounding (liquid, in our case) phase, which is a function of temperature and can have a major effect on the surface energy. Thus, temperature is one of the important parameters which play an vital role in deciding growth and kinetics of reaction during the deposition of films in CBD. Hence, in order to achieve a good deposition, optimization of temperature is a key point in CBD.

e) Doping

Doping in the starting material can be incorporated into the films only if the impurities form insoluble chalcogenides under the same condition of the deposition and provided that corresponding ionic product is greater than solubility product. The doping helps to alter the optoelectrical properties of the films.
Section 2

2.3 Introduction: Characterization Techniques for Thin Films:

To understand the diverse properties like morphology, chemical composition, optical and electrical behavior of the synthesized thin films and nano materials various characterization methods are used. The crystal phase, crystal structure and crystal size of the film samples was carried out using X-ray Diffractometer (XRD) (model: Rigaku Dmax -2400, Cu K$_\alpha$ = 0.154 nm) in the $2\theta$ range of 20 to 80°. Scanning Electron Microscope (SEM) and energy dispersive X-ray spectroscopy (EDAX) (model: JEOL-JSM 6360) was used for the morphological and average elemental composition analysis of the deposited films. UV-Visible spectrophotometer (model: JASCO V-670) was used to record optical absorption spectra of the film samples at room temperature in the diffused reflectance mode in the range of wavelength 300–800 nm. Contact angle measurement (CAM) technique was utilized in the present study to analyze the wettability of deposited films. The emission spectrum was recorded by using photoluminescence spectroscopic technique (Perkin Elmex LS55, He-Ne LASER line (325 nm) as excitation source) at room temperature.

2.3.1 X-ray Diffractometry (XRD)

X-ray diffraction (XRD) is an non-contact and non-destructive tool which helps to identify composition of material, phase of crystal, lattice parameter, crystallite size, orientation and strain state[19, 20]. Hence, it is one of the most fundamental analytical techniques in research fields like solid state physics and materials science.

2.3.1.1 Working principle

In crystal, atoms are arranged in regular repeating pattern and the smallest repeating unit is known as unit cell. The atomic planes in unit cell can act as diffracting centre, which act as 3-dimensional diffraction grating for X-rays. Therefore, given material always produces a characteristic diffraction pattern only if the X-rays scattered from ordered atomic arrangement (crystallographic planes) in a crystal interfere constructively. This can happen only if the inter atomic or inter planar distance for a given material is equal to or in order of wavelength of incident X-ray. The condition for constructive interference of X-ray due to the diffraction from crystallographic planes is given by Bragg’s diffraction law [21],

\[ 2d \sin \theta = n \lambda \]  \hspace{1cm} (2.11)
Where 'd' is lattice spacing, ‘λ’ is the wavelength of the monochromatic X-ray, ‘n’ is the order of diffraction and ‘θ’ is diffraction angle. The XRD pattern obtained for any material by this method helps to confirm whether that material is present in the pure state or as one of the constituent of a mixture of materials. Figure 2.2 shows the schematic of the Bragg action to illustrate X-ray diffraction.


**Figure 2.2** Schematic of the Bragg action to illustrate X-ray diffraction

### 2.3.1.2 Experimental

The X-ray diffraction is basically based on scattering of X-rays by the lattice. In 1912 Max von Laue discovered the diffraction of X-rays by single crystals. He found that diffraction maxima occur in particular directions which depend on the crystal structure and the wavelength. The structure determination is carried out by interpretation of the diffraction maxima. As shown in Figure 2.3, the monochromatic beam of X-ray is allowed to fall on sample. The diffracted X-rays give a pattern which provides information about atomic arrangement and hence the crystal structure and phase formation can be confirmed from XRD study. However, for other angles there should be destructive interference and hence intensity of diffracted beam will be least.
2.3.1.3 Phase identification using XRD

The X-ray diffraction pattern thus obtained is compared with Joint Committee Powder Diffraction Standards (JCPDS) powder diffraction data to identify the crystal structure and phase of the obtained product.

2.3.1.4 How it helps to determine crystallite size

Figure 2.3 Schematic of X-ray diffraction technique

Figure 2.4 shows the estimation of average crystallite size of the deposit material is estimated from the peak broadening of the peaks in the XRD-pattern of the most intense diffraction line by Scherrer’s formula is a well-known process [22]. However, the full with at half maximum, FWHM or $\beta$, need to be corrected for the instrumental broadening which is done according to equation 2.12 or by using a...
standard sample during XRD measurements,

\[ \beta = \sqrt{\beta_{\text{Measured}} - \beta_{\text{Instrument}}} \]  \hspace{1cm} (2.12)

where \( \beta \) is the measured FWHM and where \( \beta \)-instrument measured is the peak broadening due to the instrument which is the measured FWHM for a bulk sample. The average crystallite size can be measured by incorporating corrections for the strain induced broadening, using the standard method given in literature [23, 24]. As known from the literature, the equation,

\[ \beta \cos \theta = \frac{\lambda}{D} + \eta \sin \theta \]  \hspace{1cm} (2.13)

(\text{where,} \ \beta, \ \text{the full width at half maximum in radians of the diffraction peak under consideration after instrumental broadening correction,} \ \theta, \ \text{the angle of diffraction,} \ D, \ \text{size of the crystallite,} \ \eta, \ \text{is the strain in the material}) \text{ used to plot} \ \beta \ \cos \theta \ \text{Vs} \ \sin \theta. \ \text{The Y-intercept of the plot corresponds to zero strain and so eliminates the strain induced line broadening. The average crystallite size} \ D \ \text{is directly calculated from the Y-intercept}(= \frac{\lambda}{D}) \text{for each sample.}

2.3.1.5 Different XRD techniques

The way of satisfying Bragg’s condition in crystal can be devised either continuously varying \( \theta \) or \( \lambda \) during the experiment. The way in which these quantities are varied gives three different methods of diffraction; these are tabulated in Table 2.2.

Table 2.2: List of different methods of diffraction

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Method</th>
<th>Parameters</th>
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<tbody>
<tr>
<td>1</td>
<td>Laue Method</td>
<td>( \theta ) Fixed</td>
</tr>
<tr>
<td>2</td>
<td>Powder Method</td>
<td>( \theta ) Variable</td>
</tr>
<tr>
<td>3</td>
<td>Rotating crystal method</td>
<td>( \theta ) Variable (In part)</td>
</tr>
</tbody>
</table>
sample surface using high-energy electron beam. The electrons interact with the atoms in the material, producing secondary electrons, backscattered electrons, x-rays that contain information about the particle size, shape and composition, respectively. The schematic representation of SEM and its essential components are as shown in the Figure 2.5. Figure 2.6 show the photograph of SEM and EDAX system used in the present study. A typical SEM unit contains an electron gun, magnetic electron lenses, Sample stage, Vacuum chamber, Detectors for respective signals, a data output device, cooling system and power supply. Typical SEM primarily consists of an electron gun to produce an electron probe beam similar to light in optical microscope. An electron optical system comprises a set of magnetic electron lenses and deflection coils that works in tandem to produce beam of electrons that scans the surface of specimen placed on a specimen stage. It is indispensable to have high vacuum to maintain undistorted beam of electrons, where in the path of which arranged is a specimen stage that easily orients the study specimen in desired direction to have a vivid analysis. The electron beam that strikes the specimen surface produces various signals including secondary and backscattered electrons that need to be detected as shown in Figure 2.7. This is done by a set of detectors to collect respective electrons and other signals like X-rays for energy dispersive analysis of X-rays from specimen.

![Schema of construction and processes of scanning electron microscope.](image)

**Figure 2.5** Schematic of construction and processes of scanning electron microscope.

In SEM, a well-focused mono-energetic beam is made to incident on the specimen surface. This mono-energetic beam of electrons interacts with specimen producing secondary electrons and backscattered electrons which are basically used to
form specimen imaging. The intensity of backscattered electrons depends on the atomic number of host atoms. The secondary electrons are produced from the emissions of the valence electrons of constituent atoms.

**Figure 2.6** Photograph of SEM and EDAX system used in the present study.

**Figure 2.7** Schematic showing various interactions between sample and incident beam of electron.

Energy of the secondary electrons is very small and hence only those generated and emitted out from specimen surface gets detected, whereas secondary
electrons those are generated in bulk of specimen gets annihilated. Hence, these secondary electrons happen to be very sensitive to the surface of specimen, and thereby producing brightness and contrast used for image formation.

The backscattered electrons are those which get elastically scattered backwards from the host atoms. These electrons have higher energy than secondary electrons and are sensitive to the composition of the specimen. The signal produced in these set of detectors is further processed and displayed by an image display unit that provides the required view of specimen morphology.

2.3.3 Energy Dispersive X-ray Analysis (EDAX)

Energy-dispersive X-ray (EDAX) spectroscopy usually used in combination with SEM is a non-destructive technique for semi-quantitative elemental and compositional analysis for all types of solid material. In EDAX, interaction of high energy electrons with material results in production of characteristic X-rays, whose wavelengths depend on the nature of the atoms in the specimen. For the emission of the characteristic X-rays, an atom has to be excited. There by an electron from an inner shell will be knocked out. This state is unstable and the empty state will be filled up from a more energy-rich electron from an outer shell. At this relaxation, the energy difference can be released as characteristic X-ray quanta. The analysis of the energies of emitted X-ray photons provides the identities of the elements present atoms in the specimen. The volume over which the incoming electrons penetrate depends upon the accelerating voltage (i.e. the energy of the incident electron beam) and the density of the material. In typical EDAX, the incident electron beam can be focused onto a narrow region (~ 1000 Å). The X-rays generated are allowed to pass through a thin beryllium window and are detected by a reverse-biased silicon crystal. The Si detector converts the incident X-ray energies to electric pulses that are fed to suitable data acquisition system. The EDAX can detect elements with concentrations down to 0.5 wt %. It can also provide semi-quantitative compositional analysis provided, known standards are used for the comparison.

2.3.4 UV-Visible Spectroscopy: An optical absorption

Optical absorption spectroscopy is the most commonly used technique to study the electron-transition and optical band gap study of sample. The schematic diagram for a typical double beam set-up is shown in Figure 2.8. It consists of a deuterium lamp (source of UV light) and a tungsten halide lamp (source of visible light) as sources of electromagnetic radiation from 185 to 800 nm. To isolate narrow
band of wavelengths, filters and monochromators are used. A single beam from the source is divided into two beams of equal intensities which fall on sample and reference. The contribution from solvent or substrate is nullified and signal from the sample is recorded. The output signal is detected using photomultiplier tube and passed to the computer which records the spectrum.

![Schematic showing construction and working of UV-Visible spectroscope.](image)

**Figure 2.8** Schematic showing construction and working of UV-Visible spectroscope.

![Photograph of UV-vis spectrophotometer (JASCO V-670) used in the present study.](image)

**Figure 2.9** Photograph of UV-vis spectrophotometer (JASCO V-670) used in the present study.

Ultraviolet-visible (UV-vis) spectroscopy records the amount of light absorbed by elements in the sample within the ultraviolet and visible region. The UV-vis spectra record the absorption bands arising from electronic transitions within the
atoms or molecules. The molar extinction coefficient of the molecule ($\varepsilon$) can also be calculated from the absorption spectra using the Beer-Lambert Law:

$$A = \varepsilon \times c \times \ell$$

(A = absorbance, $\varepsilon$ = molar extinction coefficient, $c$ = concentration, $\ell$ = path length)

From UV-vis absorption spectrum the energy band gap of a semiconductor can be obtained, due to electron transition under irradiation. The variation of absorption coefficient, $\alpha$, with photon energy ($h\nu$) is given by 2.16:

$$(\alpha E_{\text{photon}}) = C (E_{\text{photon}} - E_g)^n$$

$$\alpha = \frac{A\ell n10}{d}$$

$$E_{\text{photon}} = \frac{1240}{\lambda \text{ (nm)}} \text{ eV}$$

Where ‘$C$’ is a constant, ‘$A$’ is the measured absorbance, ‘$d$’ is the thickness of the films and ‘$n$’ takes following values depending on the which type of transition happened :

a) $n = 1/2 \rightarrow$ direct allowed transition;

b) $n = 3/2 \rightarrow$ direct forbidden transition;

c) $n = 2 \rightarrow$ indirect allowed transition;

d) $n = 1/3 \rightarrow$ indirect forbidden transition.

For direct band gap semiconductor, extrapolation of a plot of $(\alpha h\nu)^2$ Vs $E_{\text{photon}}$ on energy axis yields an absorption energy that corresponds to a band gap $E_g$. However, in the present study (absorbance)$^2$ Vs energy plots are used for band gap calculation. There are many reports available in the literature where both the treatments are equivalent. Thus, from absorption spectra, the change in the energy band gap in semiconductor material as an effect of crystallite size can be calculated. In this work the optical absorption spectra were measured on a UV-vis spectrophotometer (JASCO V-670) over the range of 200 to 800 nm with scan rate of 200 nm/min at room temperature. Blank substrates were employed as references in transmittance mode.

2.3.5 Photoluminescence (PL) Measurement

PL is a simple, versatile, and non-destructive spectroscopic technique. The instrumentation that is required for ordinary PL work is modest: an optical source and an optical power meter or spectrophotometer. A typical PL set-up is shown in Figure
2.11.

Figure 2.10 Schematic diagrams for (a) direct and (b) Indirect band gap semiconductors.

The luminescence measurement does not rely on electrical excitation or detection also; the sample preparation is minimal which makes PL particularly attractive for material systems having poor conductivity or undeveloped contact/junction technology.

Figure 2.11 The schematic of typical experimental set-up for photoluminescence measurement.

Photoluminescence (PL) is one of the very important tools. Indeed PL analysis
is a non-destructive technique requires very less sample preparation. When light of sufficient energy is made incident on a material, photons are absorbed and electronic excitations are created. After completing the life time, these excitations relax and the electron returns to the ground state. If the state is radiative, it will generate unique peaks in the PL spectrum. Thus, the PL measurement is a very sensitive and selective probe of such states. PL investigations can be used to characterize a variety of material parameters. PL spectroscopy provides electrical (as opposed to mechanical) characterization, and it is a selective and extremely sensitive probe of discrete electronic states. Features of the emission spectrum can be used to identify surface, interface, and impurity states and to gauge alloy disorder and interface roughness. The intensity of the PL signal provides information on the quality of surfaces and interfaces. In addition to identifying discrete states, PL peak positions can be used to evaluate the composition of semiconductor alloys.

![Figure 2.12 Schematic diagram showing (a) band to band (b) donor to valence band (c) conduction band to acceptor and (d) non-radiative recombination.](image)

**2.3.6 Contact angle measurement**

Typically, contact wetting angle measurement is qualitatively used to detect synthesis parameter-induced surface changes by classifying surfaces as hydrophobic or hydrophilic (Figure 2.13). Contact angle measurement is a simple, inexpensive and an empirical diagnostic tool for evaluating wettability of surface as a function of different preparative parameters. The interaction of liquids and solids of different surface energies are known to give rise to the formation of characteristic angles known as contact wetting angles at a liquid/solid/vapor interface [34]. The contact angle is specific for any given system and depends upon the interactions between the
three interfaces.

**Figure 2.13** Schematic of contact angle measurement illustrating surface wettability of Films.

**Figure 2.14** Photograph of contact angle measurement set-up used in present study.

Figure 2.13 and 2.14 shows the schematic illustration of the contact angle and the interfacial tensions. The Young’s equation gives the relationship between contact angle $\theta$, liquid-vapor surface tension $\gamma_{lv}$, solid-vapor surface tension $\gamma_{sv}$, and solid-liquid surface tension $\gamma_{sl}$ and it is expressed as [35, 36]:

$$\gamma_{sv} - \gamma_{lv} = \gamma_{sl} \cos \theta$$
\[ \gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sf} \] (2.18)

Most often, if the liquid is strongly attracted by the solid surface, then droplet will completely spread out on the solid surface and the contact angle will be closed to zero indicating that the surface will be super hydrophilic. Less strongly hydrophilic solids will have contact angle up to 90°, whereas many highly hydrophobic surfaces have water contact angles as high as around 120° on low energy materials e.g. fluorinated surfaces. However, some materials with highly rough surfaces may have water contact angle greater than 150°. These are called as super hydrophobic surfaces. On these surfaces, the water droplets simply rest without actually wetting with surface to any significant extent.

Films wettability is an important property for semiconductor sensitized solar cells (SSSC) since the pores of metal oxide films should be filled and covered at maximum with the sensitizer in order to increase the absorption.

2.4 Solar spectrum, irradiation and Solar cell characteristics

The efficiency of solar cell is function of the intensity and the energy distribution of the incident light. Therefore, it is necessary to define a standard spectrum and power density in order to allow for an accurate comparison among different photovoltaic devices. The Sun emits light resembling the spectrum of a blackbody at a temperature of 5670 K (Figure 2.15).

![Schematic of solar spectrum irradiation](http://www.sbs.net.au/science/articles/2013/10/06/3864474.htm)

**Figure 2.15** Schematic of solar spectrum irradiation
Before reaching the ground, the radiation passes through the atmosphere, which modifies the solar spectrum, both intensity and energy distribution. The radiation that finally reaches the ground will depend on the length of the path the radiation must follow. This optical path is known as Air Mass (AM). The AM is defined as,

\[ AM = \frac{1}{\cos(\theta)} \]  

(2.19)

Where \( \theta \) is the angle of elevation of the Sun (Figure 2.16). The accepted standard for solar cell testing is the so called AM 1.5, which is a 100 mW/cm\(^2\) white light intensity with a spectral intensity distribution matching that of the Sun on the earth’s surface tilted at an angle of 37°.

**Fig. 2.16** The path length in units of Air Mass, changes with the zenith angle.

**Figure 2.17** Schematic of J-V curve used to characterize SSSC.
The electrical performance of a solar cell is determined from the current-voltage (I-V) correlation obtained on illuminating the cell with a solar simulator calibrated at AM1.5 solar spectrum. From the I-V curve, the short-circuit current density $J_{sc}$, the open-circuit voltage, $V_{oc}$ and the fill factor, $FF$ are obtained as illustrated in Figure 2.17. The solar cell collection efficiency, $\eta$ which is a measure of the fraction of the solar energy incident on the cell that is converted into electrical energy is determined from the cell external parameters as:

$$\eta = \frac{J_{sc} \cdot V_{oc} \cdot FF}{P_{in}}$$  \hspace{1cm} (2.20)

Where $P_{in}$ is the input power of AM 1.5 spectrum.

In SSSC, the open-circuit voltage defines the voltage beyond which the solar cell no longer provides power. It’s the difference between the Fermi energy level of metal oxide and the redox potential of the electrolyte. However, such a modification increases the optical band-gap of the donor material and consequently the maximum attainable $J_{sc}$ will be reduced. In order to balance photocurrent and the maximum attainable voltage from the device (and thus maximize device PCE), the band gap of the active semiconducting layer should be between 1.3 and 1.5 eV. Energy losses associated with charge-transfer states preceding free charge generation, recombination of charge carriers, and quality of electrode-electrolyte interfaces reduce the practically attainable $V_{oc}$. The value of short circuit current density is determined by the amount of light absorbed by the sensitizer and the ability of the device to carry the generated charge to the FTO surface. The $FF$ is a quantity, with value lies between 0 and 1, being closer to unity for devices in which charge mobility in both the sensitizer (donor) and metal oxide photoanode (acceptor) phases are high, balanced, and recombination rates are low. It is a measure of the ‘squareness’ of the I-V curve and describes the degree to which the voltage at the maximum power point ($V_{max}$) matches $V_{oc}$ and current density at the maximum power point ($J_{max}$) matches $J_{sc}$.
References


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