Thin Film Deposition and Characterization Techniques

Chapter 2

Thin Film Deposition and Characterization Techniques

2.1. Deposition of Tin Oxide Films

A wide range of technological applications use tin oxide in porous ceramics, such as gas sensors, burglar alarms, catalysts and in dense, highly transparent and conductive tin oxide films [1–4], as electrodes for solar cells, liquid crystal displays (LCDs), electrochromic displays (ECDs) [5–9], heating elements in aircraft, special furnaces, and luminescent lamps [10,11]. The optical and electrical properties of SnO$_2$ depend on several factors such as the methodology used to prepare the film & its processing temperature. These factors directly influence the film’s morphology and indirectly its applications.

To optimize its properties, foreign atoms can be incorporated into the crystal lattice of SnO$_2$ to promote, for example, increased electrical conductivity by increasing defect concentration or by forming additional states of the optical band gap [12].

Several methods which have been developed to obtain suitable conducting SnO$_2$ layers after McMaster [13] devised the first successful process are: sputtering methods (r.f or d.c, reactive or non-reactive) [14 – 16], evaporation methods [17] and chemical vapour deposition [18,19]. These are expensive and have certain disadvantages for mass production. Apart from these deposition methods, spray pyrolysis systems are easy to fabricate and cost effective. Because of the simplicity of the deposition apparatus, it can be easily modified for mass production. The films deposited by this technique are fairly uniform with mobilities ranging from $10^{-2}$ to $10^{-3}$ Vcm$^{-1}$ with an average optical transmission of above 80% in the visible region.
The films also have excellent reproducibility. In the present work, undoped and antimony doped tin oxide films have been grown on glass plates and the effect of various process parameters on the film properties have been studied to develop these materials as indigenous & low cost.

2.1.1. Antimony Doped Tin Oxide Thin Films by Spray Pyrolysis

Stannic chloride anhydrous (SnCl\textsubscript{2}) from spectrochem (India) and antimony trichloride (SbCl\textsubscript{3}) of AR grade purchased from sd-fine chemicals (India) were used as precursors for tin and antimony, respectively. Isopropanol and HCl were purchased from sd-fine and were used without further purification.

Two types of antimony doped samples were deposited, one is lower percentage of antimony doping (1, 2, 3, 4 wt %) and another higher percentage of antimony doping (8, 10, 20, 30, 40, 50 wt %).

Firstly, 0.2 M of SnCl\textsubscript{2} is added to isopropanol and the solution is kept for continuous stirring; HCl is added drop by drop till a clear solution is obtained. The undoped SnO\textsubscript{2} films were prepared by spraying the above solution on properly cleaned glass slides at temperature 500 °C in open conditions. This is done using our home built spray setup that is shown in Fig. 2.1. The specially designed atomizer made of teflon fitted in borosil conical flask was used. The advantage of this setup is that contamination of spray solution that typically occurs in a commercial setup which is usually made up of metal components can be prevented. For antimony doping, SbCl\textsubscript{3} was added to the above starting solution in the range 1-4 wt% for lower Sb doping and 8–50 wt% for higher doping in comparison to SnCl\textsubscript{2}. Films of 1-4 wt% and 8, 10, 20, 30, 40, 50 wt% Sb doped SnO\textsubscript{2} were prepared. In each case, 50 ml of starting solution is sprayed to maintain uniform thickness of films of different composition. For 1 to 4 wt% Sb doping the colour of films was almost transparent.
Figure 2.1: A schematic diagram of the Spray pyrolysis set up. (1) Spray solution (2) Atomizer (3) Spray nozzle (4) Droplet transport (5) Substrate (6) Steel plate (7) Heater (8) Power supply (9) Thermocouple (10) Pressure regulator.

For higher Sb doping from 8-50 wt%, as the concentration of Sb doping increases, the colour of films turned from almost colourless (transparent) to dark bluish in colour. These films were then allowed to cool at room temperature and were further used for structural, optical and electrical characterizations.

2.2. Deposition of Cadmium Sulphide Thin Films

Cadmium sulphide (CdS) thin films have received growing interest over the past three decades due to their opto-electrical properties, which are suitable for photovoltaic cell as window layers [20-23], photodiode [24], gas sensors [25], and photoconductive sensors [26]. It is one of the metal chalcogenide semiconductors (II-VI) used in solar cells due to its wide and direct band gap transition (2.42eV), high index of refraction (2.5), high absorption coefficient, high photoconductivity and n-type conductivity. It
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is an excellent heterojunction partner for p-type CdTe, CuInSe$_2$, Cu(In,Ga)Se$_2$ (CIGS) because of the wide optical band gap. Various methods employed for depositing CdS thin films are screen printing [27], Sol-Gel [28], Successive Ionic Layer Absorption & Reaction (SILAR) [29], chemical vapour deposition [30], electrodeposition [31], atmospheric pressure metal-organic chemical vapour deposition (AP-MOCVD) [32], automated low cost trigger enhanced spray (TES) technique [33], electrostatic spray assisted vapour deposition (ESAVD) [34], spray pyrolysis [35], flash evaporation [36] and chemical bath deposition (CBD) [37-40] technique. Of the various methods, CBD technique has many advantages such as simplicity, no requirement for sophisticated instruments, minimum material wastage, and economical way of large area deposition.

2.2.1. Chemical Bath Deposition of Cadmium Sulphide Thin Films

Cadmium sulphide thin films were deposited by CBD using two complexing agents, (a) Triethanolamine and (b) Ammonia.

All the chemicals used in the present work were of analytical grade, cadmium chloride monohydrate (CdCl$_2$H$_2$O), cadmium acetate, cadmium iodide, cadmium nitrate obtained from (Himedia), thiourea NH$_2$.CS.NH$_2$ (Thomas Baker), ammonia solution 25% and triethanolamine (sd-Fine Chemicals, India) (Sigma-Aldrich) and were used for the deposition of cadmium sulphide thin film by CBD. All the solutions were prepared by dissolving appropriate quantity of material into de-ionized water.

In case of triethanol amine, the chemical bath has been set to deposit CdS films using cadmium chloride and thiourea as a source of cadmium and sulphur ions respectively. Prior to optimizing the bath conditions, a large number of trails for different conditions with respect to temperature, concentration of ions and pH were carried out. The condition that yielded superior films, with respect to continuity, smoothness and
adherence, was chosen to deposit the final films for further studies. A brief recipe of the present deposition is as follows. The substrates used to deposit films are both commercial glass slides and ITO coated glass slides (Xin Yan Technology LTD, Hong Kong) of typical size $70 \times 25 \text{ mm}^2$. Prior to deposition the glass slides were cleaned by standard procedure. First it was cleaned with soap solution then boiled in soap solution for 30 minutes and finally rinsed with copious amount of distilled water and followed by sonication in water for 10 minutes. In two separate beakers, the
solution of cadmium acetate, iodide, chloride and nitrate (5 mM) and Thiourea (10 mM) were prepared. Triethanolamine was added to cadmium solution under constant stirring till a white precipitate of Cd(OH)$_2$ gets dissolved and the solution becomes clear, here triethanolamine also acts as a complexing agent in the chemical bath. The measured pH of final solution was close to 11.5. Quickly the solution of thiourea was added to the solution of cadmium in 100 ml beaker under stirring and the temperature of solution was raised to 60 °C, a special heat bath is designed to achieve a uniformly heating of bath well above the solution level in the beaker. The set used to deposit the CdS thin films is shown Fig. 2.2. Once the required temperature is reached the cleaned glass/ITO slides were inserted vertically along the wall of the beaker and are left undisturbed for chemical bath deposition of CdS films for two hours. Initial colourless solution starts turning slowly to pale yellow with time and at the end of required time a clear deposition of CdS is observed both on glass slides and on the wall of beaker. The deposited slides were cleaned thoroughly with distilled water and later sonicated to remove unadherent material, finally these slides were dried for further characterization. The resulting films were yellowish, homogeneous, spectacularly reflecting with good adherence. CdS thin films using ammonia as complexing agent were also deposited by following same procedure where we have used cadmium chloride as Cd source and thiourea as sulphur source.

2.2.2. Solution Phase Doping of as Prepared CdS Films

Cadmium chloride monohydrate (CdCl$_2$.H$_2$O), lead nitrate (Pb$_2$NO$_3$) and copper (II) chloride dehydrate (CuCl$_2$.2H$_2$O) were obtained from (Himedia), thiourea NH$_2$.CS.NH$_2$ (Thomas Baker), ammonia solution 25% (sd-Fine Chemicals, India) and silver nitrate (Sigma-Aldrich) were used for the deposition of cadmium sulphide thin
film by CBD. All the solutions were prepared by dissolving appropriate quantity of material into de-ionized water.

The solution phase doping of CdS films was studied by immersing these films in different cationic solutions at ambient condition. 5 mM solution of Pb, Cu and Ag were prepared using Pb(NO₃)₂, CuCl₂·H₂O and AgNO₃, respectively in water. Then as deposited CdS films were completely immersed in these solutions at room temperature for a duration (5 minute) to ensure that there is saturated diffusion of cations, as a result the original films are completely doped. At the end of this, films were thoroughly washed with distilled water and dried in air for further measurements. It is important to note that the solution doping clearly shows visible change in the colour of original film.

2.2.3. Passivation of Thiol Molecules on CdS Surface

All the chemicals used in the present work were of analytical grade, cadmium chloridemonohydrate (CdCl₂·H₂O), obtained from (Himedia), thiourea NH₂·CS·NH₂ (Thomas Baker), ammonia solution 25% (sd-Fine Chemicals, India) and silver nitrate Dodecane thiol, 1-Heptanethiol, 1-Octadecanethiol were used from Sigma-Aldrich. All the solutions were prepared by dissolving appropriate quantity of material into de-ionized water.

CdS films were deposited using cadmium chloride, thiourea and ammonia as complexing agent. The as deposited films were removed from the chemical bath, sonicated well and dried in open air. These films treated separately by each thiol as follows, the dried CdS sample was placed in three different covered Petri dish. One drop of each thiol was pipetted in 5 ml ethanol in each petri dish and whole solution was pipetted onto the sample surface, making sure to cover the entire film in petri dish. After five minutes, the treatment solution was poured off and the samples were
thoroughly washed with ethanol & then dried at room temperature. Current- Voltage (I-V) measurements were performed using a Keithley 617 programmable electrometer that is interfaced with computer.

2.3. Thermal Oxidation Synthesis of Cupric Oxide

All the chemicals used in the present work were of analytical grade, copper metal powder was obtained from (Himedia), Diethylenetriamine (DETA) (C_2H_13N_2) and Oleylamine (OA) (C_{18}H_{37}N) were obtained from (sd-Fine Chemicals, India). Thermal oxidation of pristine copper powder and chemically treated copper powder with amine has been carried out. Thermal oxidation was carried out in a muffle furnace for period of about 60 minute at high temperature. Copper metal powder (99.99% ) purity, was used as the starting material. The copper powder was loaded into the crucible, which was then placed in a conventional muffle furnace for thermal oxidation under open conditions. Here heating was carried out at two different temperature one at 500 °C and another at still higher temperature that is 700 °C. After heating, the copper powder gets converted into gray/black material that was collected stored for further characterization (Fig 2.3). Surface morphology of these powders was characterized by scanning electron microscopy (SEM) (JSM-5900) operated at 30 kV.

Figure 2.3: A process of thermal oxidation of copper to get Copper Oxide.
The crystal structure and phase analysis was done by using powder X-ray diffraction (Rigaku smartlab X-ray diffractometer) using a CuK\(_{\alpha}\) radiation (\(\lambda = 1.5417 \, \text{Å}\)).

Similarly, amine treated copper powder is also subjected to oxidation. Here the required amount of copper powder was ground sequentially for six hours with DETA and OA to achieve the through mixing and reaction. Again the amine treated copper was fired at 500 °C and 700 °C for 60 min in open conditions. After annealing the powder were collected and washed thoroughly with copious amount of double distilled water and dried, this material is used for further characterization.

2.4. Characterization Techniques

Various characterization techniques like X-ray diffraction, thin film metrix, optical absorption spectroscopy, scanning electron microscopy and the electrical conductivity measurement are used to characterize the present materials and hence these will be discussed here.

2.4.1. X-Ray Powder Diffraction

2.4.1.1. Introduction

X-rays are electromagnetic radiation with typical photon energies in the range of 100 eV - 100 keV. For diffraction applications, only short wavelength X-rays (hard X-rays) in the range of a few angstroms to 0.1 angstrom (1 keV - 120 keV) are used. Because the wavelength of X-rays is comparable to the size of atoms, they are ideally suited for probing the structural arrangement of atoms and molecules in a wide range of materials. The energetic X-rays can penetrate deep into the materials and provide information about the bulk structure. X-rays are produced generally by either X-ray tubes or synchrotron radiation. In a X-ray tube, which is the primary source used in laboratory, these are generated when a focused electron beam accelerated across a high voltage field bombards a stationary or rotating solid target. As electrons collide
with atoms in the target and slow down, a continuous spectrum of X-rays are emitted, which are termed Bremsstrahlung radiation. The high energy electrons also eject inner shell electrons in atoms through the ionization process. When a free electron fills the shell, a X-ray photon with energy characteristic of the target material is emitted. Common targets used in X-ray tubes include Cu and Mo, which emit 8 keV and 14 keV X-rays with corresponding wavelengths of 1.54 Å and 0.8 Å, respectively. In recent years synchrotron facilities have become widely used as preferred sources for X-ray diffraction measurements. Synchrotron radiation is emitted by electrons or positrons travelling at near light speed in a circular storage ring. These powerful sources, which are thousands to millions of times more intense than laboratory sources, have become indispensable tools for a wide range of structural investigations and brought advances in numerous fields of science and technology.

X-rays primarily interact with electrons in atoms. When X-ray photons collide with electrons, some photons from the incident beam will be deflected away from the direction where they original travel, much like billiard balls bouncing off one another. If the wavelength of these scattered X-rays did not change (meaning that X-ray photons did not lose any energy), the process is called elastic scattering (Thompson Scattering) in that only momentum has been transferred in the scattering process. These are the X-rays that we measure in diffraction experiments, as the scattered X-rays carry information about the electron distribution in materials. On the other hand, in the inelastic scattering process (Compton Scattering), X-rays transfer some of their energy to the electrons and the scattered X-rays will have different wavelength than the incident X-rays. Diffracted waves from different atoms can interfere with each other and the resultant intensity distribution is strongly modulated by this interaction. If the atoms are arranged in a periodic fashion, as in crystals, the diffracted waves will
consist of sharp interference maxima (peaks) with the same symmetry as in the
distribution of atoms. Measuring the diffraction pattern therefore allows us to deduce
the arrangement of atoms in a material. The peaks in a X-ray diffraction pattern are
directly related to the atomic distances. The Bragg's law \(2d \sin \theta = n\lambda\), where \(d\) is the
interplaner spacing of set of parallel planes, \(\theta\) is the scattering angle, one of most
important law used for interpreting X-ray diffraction data.

2.4.1.2. Schematic of X-Ray Diffractometer

Structure of thin films can be amorphous, polycrystalline or epitaxial, and the films
can be prepared as a single layer films, multilayers or as a graded films. Main
differences in structure of thin films with respect to the powder samples are given by
a singular direction of their growth, by their adhesion to a substrate and often also by
a simultaneous bombardment by atomic species during the growth.

A complete structure analysis of thin films by means of X-ray diffraction
(XRD) usually needs more than one diffraction geometry to be used and some of
these are, (a) Bragg-Brentano (0-20) geometry, (b) Grazing incidence geometry, (c)
Reflectivity, (d) Rocking curve, (e) "Thin film" geometry etc. The mostly used
diffraction geometry, the "Thin Film" (TF) geometry, is the geometry in which the
incident beam makes a fixed and generally small angle (less than 10°) with the sample
surface and the detector moves along a circle centred at the sample position. This is
asymmetric diffraction geometry because the angle of the incident beam and the
registered diffracted beam with respect to the sample surface are different. In this case
the reflections originate from different sets of grains which have crystallographic
planes that are inclined at different angles with respect to the sample surface. The
higher is the angular position of the detector, the higher is the angle of tilt of
diffracting planes. This method is convenient for the characterisation of thin film, because the substrate signal does not interfere with the film signal.

Generally speaking, thin film diffraction refers not to a specific technique but rather a collection of XRD data to characterise thin film samples grown on substrates. These materials have important technological applications in microelectronic and optoelectronic devices, where high quality epitaxial films are critical for device performance. Thin film diffraction methods are used as important process development and control tools, as hard X-rays can penetrate through the epitaxial layers and measure the properties of both the film and the substrate. A simple Bragg-Brentano geometry is shown in Fig. 2.4

![Figure 2.4: Schematic of X-ray diffractometer](image_url)
The basic geometry of an X-ray diffractometer involves a source of monochromatic radiation and an X-ray detector situated on the circumference of a graduated circle centered on the powder specimen. Divergent slits, located between the X-ray source and the specimen, and divergent slits, located between the specimen and the detector, limit scattered (non-diffracted) radiation, reduce background noise, and collimate the radiation. The detector and specimen holder are mechanically coupled with a goniometer so that a rotation of the detector through 2x degrees occurs in conjunction with the rotation of the specimen through x degrees, a fixed 2:1 ratio.

Figure 2.5: Optical arrangement for a X-ray Diffractometer

A curved-crystal monochromator containing a graphite crystal is normally used to ensure that the detected radiation is monochromatic (Fig 2.5). When positioned properly just in front of the detector, only the K-alpha radiation is directed into the detector, and the K-beta radiation, because it is diffracted at a slightly different angle, is directed away. The signals from the detector are filtered by pulse-height analysis, scaled to measurable proportions, and sent to a linear ratemeter for conversion into a continuous current. Common output devices include strip-chart recorders, printers, and computer monitors.

In the present study X-ray diffraction patterns were recorded on CdS and antimony doped tin oxide thin films by using Ultima-4 Rigaku X-ray diffractometer, operating
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at 25 kV and 20 mA with Cu Kα radiation (1.54056 Å) and a typical scanning rate of 0.01°/s.

The Debye-Scherrer’s formula is used in the study of crystalline particle size using X-ray diffraction, this formula relates the size of crystal particle to the full width half maxima (fwhm) of diffracted peak [41-43]. It is given by

\[ d = \frac{k\lambda}{\beta \cos \theta} \]  (2.1)

Where \( d \) is the particle diameter, \( \lambda \) is the wavelength of X-ray used, \( \beta \) is the full width at half maximum of a diffracted peak, \( \theta \) is the scattering angle, \( K \) is constant that is equal to 0.89, which is related both to the crystallite shape and to the way in which \( \beta \) & \( d \) are defined.

2.4.2. Thickness Measurement

Films typically used in thin-film applications range from a few atoms (<10Å or 0.0001 μm) to 100 μm thick (twice the width of a human hair.) They can be formed by many different processes, including spin coating, vacuum evaporation, sputtering, vapor deposition, and dip coating etc. To perform the functions for which they were designed, thin films must have the proper thickness, composition, roughness, and other characteristics that are important for the particular applications. These characteristics must often be measured, both during and after thin film fabrication. The two main classes of thin film measurement are optical and stylus based techniques. Stylus measurements measure thickness and roughness by monitoring the deflections of a fine tipped stylus as it is dragged along the surface of the film. Stylus instruments are limited in speed and accuracy, and they require a “step” in the film to measure thickness. They are often the preferred and better suited methods when measuring opaque films, such as metals etc.
Optical techniques determine thin-film characteristics by measuring how the films interact with light. Optical techniques can measure the thickness, roughness, and optical constants of a film. Optical constants describe how light propagates through and reflects from a material. Once known, optical constants may be related to other material parameters, such as thickness and band gap.

**Figure 2.6: Filmtrics Block Diagram**

Optical techniques are usually the preferred method for measuring thin films because they are nondestructive, require little or no sample preparation and are as accurate as stylus methods. But the disadvantage is the optical parameters of material under investigation must be known more accurately. The two most common optical measurement types are spectral reflectance and ellipsometry. Spectral reflectance measures the amount of light reflected from a thin film over a range of wavelengths, with the incident light normal (perpendicular) to the sample surface. Ellipsometry is similar, except that it measures reflectance at non-normal incidence and at two
different polarizations. In general, spectral reflectance is much simpler and less expensive than ellipsometry, but it is restricted to measuring less complex structures.

The Optical constants (n and k where n is the refractive index & k is the dielectric constant) describe how light propagates through a film. In simple terms, the electromagnetic field that describes light traveling through a material at a fixed time is given by:

$$A \cdot \cos \left( \frac{2\pi}{\lambda} x \right) \cdot \exp \left( - K \frac{2\pi}{\lambda} x \right) \quad \text{(2.2)}$$

where x is distance, $\lambda$ is the wavelength of light, and n and k are the film's refractive index and extinction coefficient, respectively. The refractive index is defined as the ratio of the speed of light in a vacuum to the speed of light in the material. The extinction coefficient is a measure of how much light is absorbed in the material.

Reflection occurs whenever light crosses the interface between different materials. The fraction of light that is reflected by an interface is determined by the discontinuity in n and k. For light reflected off of a material in air

![Diagram of light reflection](image)

**Figure 2.7**: Reflection of light at the interface between two different materials
To see how spectral reflectance can be used to measure optical constants, consider the simple case of light reflected by a single nonabsorbing material (k=0).

Then:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$  \hspace{1cm} (2.3)

Clearly, $n$ of the material can be determined from a measurement of $R$. In real materials, $n$ varies with wavelength (that is to say, real materials exhibit dispersion), but since the reflectance is known at many wavelengths, $n$ at each of these wavelengths is also known, as shown here.

**Figure 2.8:** Single nonabsorbing material on which the variation of reflection and refraction index with wavelength are shown.

Next, consider now a thin film on top of another material. In this case both the top and bottom of the film reflect light. The total amount of reflected light is the sum of these
two individual reflections. Because of the wavelike nature of light, the reflections from the two interfaces may add together either constructively (intensities add) or destructively (intensities subtract), depending upon their phase relationship.

![Diagram of light reflection](image)

**Figure 2.9:** The reflection of incident light from the multiple interfaces.

Their phase relationship is determined by the difference in optical path lengths of the two reflections, which in turn is determined by thickness of the film, its optical constants, and the wavelength of the light. Reflections are in-phase and therefore add constructively when the light path is equal to one integral multiple of the wavelength of light. For the perpendicularly incident of light on a transparent film, this occurs when, where $d$ is the thickness of the film and $i$ is an integer (the factor of two is due to the fact that the light passes through the film twice). Conversely, reflections are out of phase and add destructively when the light path is one half of a wavelength.
different from the in-phase condition, or when the qualitative aspects of these reflections may be combined into a single equation:

\[ R \approx A + B \cos \left( \frac{2\pi}{\lambda} nd \right) \]  \hspace{1cm} (2.5)

From this, we can see that the reflectance of a thin film will vary periodically with 1/wavelength. Also, thicker films will exhibit a greater number of oscillations over a given wavelength range, while thinner films will exhibit fewer oscillations, and often times only part of an oscillation, over the same range. In our work, thickness of different CdS and Antimony doped Tin Oxide (ATO) thin films was measured by thin filmetrics (F20-UV thin- film analyzer).

### 2.4.3. Scanning Electron Microscopy (SEM)

There are a wide range of analytical techniques which may be used for materials characterization depending on the type of information needed. For high resolution surface investigations, two commonly used techniques are Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). Each of these techniques resolves surface structure down to the nanometer scale. However, the image formation mechanisms are quite different, resulting in different types of information about the surface structure. The occurrence of the SEM and AFM side-by-side is becoming more common in today's analytical laboratories.

The first SEM was constructed in 1938 by von Ardenne by rastering the electron beam of a Transmission Electron Microscope (TEM) to essentially form a Scanning Transmission Electron Microscope (STEM). In 1942, Zworkin et. al. developed the first SEM for bulk samples. This configuration contains many of the basic principles of today's SEMs. Cambridge Scientific Instruments produced the first commercial instrument in 1965. A number of improvements have occurred since this time, resulting in an increase in resolution from 50 nm in 1942 to ~ 0.7 nm today.
Besides the development of morphological imaging, the SEM has been developed to detect signals which are used to determine compositional information, such as X-rays.

**Figure 2.10:** Schematic Diagram of Scanning electron microscope
backscattered electrons, cathodoluminescent, Auger electrons, and electron beam induced specimen current. The operation of the SEM consists of applying a voltage between a conductive sample and filament, resulting in electron emission from the filament that is accelerated by large electric field so that the beam can be focused to the sample surface with very small size. This occurs in a vacuum environment ranging from $10^{-4}$ to $10^{-10}$ Torr. The electrons are guided to the sample by a series of electromagnetic lenses in the electron column. A schematic of a typical SEM is shown in Fig. 2.10.

The resolution and depth of field of the image are determined by the beam current and the final spot size, which are adjusted with one or more condenser lenses and the final, probe-forming objective lenses. The lenses are also used to shape the beam to minimize the effects of spherical aberration, chromatic aberration, diffraction, and astigmatism.

The electrons interact with the sample within a few nanometers to several microns of the surface, depending on beam parameters and sample type. Electrons are emitted from the sample primarily as either backscattered electrons or secondary electrons. Secondary electrons are the most common signal used for investigations of surface morphology. They are produced as a result of interactions between the beam electrons and weakly bound electrons in the conduction band of the sample. Some energy from the beam electrons is transferred to the conduction band electrons in the sample, providing enough energy for their escape from the sample surface as secondary electrons. Secondary electrons are low energy electrons (<50eV), so only those formed within the first few nanometers of the sample surface have enough energy to escape and be detected. High energy beam electrons which are scattered back out of the sample (backscattered electrons) can also form secondary electrons.
when they leave the surface. Since these electrons travel farther into the sample than the secondary electrons, they can emerge from the sample at a much larger distance away from the impact of the incident beam which makes their spatial distribution larger. Once these electrons escape from the sample surface, they are typically detected by an Everhart-Thornley scintillator photomultiplier detector. The SEM image formed is the result of the intensity of the secondary electron emission from the sample at each x, y data point during the rastering of the electron beam across the surface. In the present work SEM measurements are carried out using Jeol JSM 6360 scanning electron microscope with operating voltage up to 30 kV. The Magnification upto 3,00,000 can be achieved that is Fully computer controlled.

2.4.4. Energy Dispersive Spectrometer

Energy-dispersive X-ray spectroscopy (EDS, EDX, or XEDS), sometimes called energy dispersive X-ray analysis (EDXA) or energy dispersive X-ray microanalysis (EDXMA), is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray spectrum. To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of charged particles such as electrons or protons, or a beam of X-rays, is focused into the sample being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was occupied. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and
the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer.

![Schematic of a Energy Dispersive Spectrometer](image.jpg)

Figure 2.11: Schematic of a Energy Dispersive Spectrometer for specially resolved chemical analysis

As the energy of the X-rays are characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured.

The central component of an EDS system is a solid-state detector, consisting of semiconductor devices. As each X-ray photon hits the detector, a very small current is produced by knocking out electrons from the semi-conductor. Each electron ejected from a silicon electron shell consumes about 3.8 eV of energy from the X-ray. Therefore an X-ray photon starting with 7,471 eV of energy (Ni Ka) will produce a current of about 1,966 electrons. By measuring the amount of current produced by
each X-ray photon, the original energy of the X-ray can be calculated. An EDS spectrum is essentially a histogram of the number of X-rays measured at each energy.

### 2.4.5. Optical Absorption Measurements

The instrument used in ultraviolet-visible spectroscopy is called a UV/Vis spectrophotometer. It measures the intensity of light passing through a sample \( (I) \), and compares it to the intensity of light before it passes through the sample \( (I_0) \).

The ratio \( I/I_0 \) is called the transmittance, and is usually expressed as a percentage \( (\%T) \). The absorbance, \( A \), is based on the transmittance: \( A = -\log(\%T/100\%) \).

The UV-visible spectrophotometer can also be configured to measure reflectance. In this case, the spectrophotometer measures the intensity of light reflected from a sample \( (I) \), and compares it to the intensity of light reflected from a reference material \( (I_0) \). The ratio \( I/I_0 \) is called the reflectance, and is usually expressed as a percentage \( (\%R) \).

![Block Diagram of Spectrophotometer](image)

**Figure 2.12:** Block Diagram of Spectrophotometer depicting the significance of various components.
The basic parts of a spectrophotometer are the light source, a holder for the sample, a diffraction grating in a monochromator or a prism to separate the different wavelengths of light, and a detector to measure the transmitted light. The block diagram of UV-absorption spectrometer is shown in figure 2.11. The radiation source is often a tungsten filament (300-2500 nm), a deuterium arc lamp, which is continuous over the ultraviolet region (190-400 nm), Xenon arc lamp, which is continuous from 160-2,000 nm; or more recently, light emitting diodes (LED) for the visible wavelengths are also used. The detector is typically a photomultiplier tube, a photodiode, a photodiode array or a charge-coupled device (CCD). Single photodiode detectors and photomultiplier tubes are used with scanning monochromators, which filter the light so that only light of a single wavelength reaches the detector at one time. The scanning monochromator moves the diffraction grating to "step-through" each wavelength so that its intensity may be measured as a function of wavelength. Fixed monochromators are used with CCDs and photodiode arrays. As both of these devices consist of many detectors grouped into one or two dimensional arrays, they are able to collect light of different wavelengths on different pixels or groups of pixels simultaneously.

A spectrophotometer can be either single beam or double beam. In a single beam instrument, all of the light passes through the sample cell. \( I_0 \) must be measured by removing the sample. This was the earliest design and is still in common use in both teaching and industrial labs.

In a double-beam instrument, the light is split into two beams before it reaches the sample (Figure 2.12). One beam is used as the reference; the other beam passes through the sample. The reference beam intensity is taken as 100% Transmission (or 0 Absorbance), and the measurement displayed is the ratio of the two beam intensities.
Some double-beam instruments have two detectors (photodiodes), and the sample and reference beam are measured at the same time. In other instruments, the two beams pass through a beam chopper, which blocks one beam at a time. The detector alternates between measuring the sample beam and the reference beam in synchronism with the chopper. There may also be one or more dark intervals in the chopper cycle. In this case, the measured beam intensities may be corrected by subtracting the intensity measured in the dark interval before the ratio is taken.

In the present work all optical measurements were performed in the wavelength range 300-1100 nm using Analytikjena Specord 200 plus (Germany). The optical absorption were recorded on pure CdS, CdS:Pb, CdS:Ag and CdS:Cu to calculate critical absorption wavelength and energy gap of these semiconductors. Absorption spectra of un-doped, antimony doped SnO\textsubscript{2} thin films deposited on glass slides, was also recorded to study surface plasmon resonance phenomenon.

2.4.6 Electrical Characterization

Electrical conductivity of the films was measured by our home built two probe set up with soft electrical contacts, the two metal probes (stripes: 4 mm length, 0.7mm width and 0.38 mm separation between the probes) loaded on a soft polymer pad (PDMS) that further loaded with spring pressure rests on film surface, the setup a convenient method to measure electrical conductivity of soft materials, a lower version of this setup has been published by us elsewhere [41].
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REFERENCES

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