CHAPTER-III

EXPERIMENTAL DETAILS
Chapter-3

EXPERIMENTAL DETAILS

The details of experimental methods are described in this chapter. The whole description can be divided into the following three sections:

3.1 Preparation of photoconductive materials,

3.2 Thickness determination and

3.3 Measuring arrangements.

Now we will describe them one by one.

Photoconductors can be prepared in different forms like powders, crystals or thin films etc. The different preparational techniques used for such materials are described in the following lines:

3.1.1 Powders

(i) Powder Firing Technique:

In this technique, a mixture of the ingredients like base, dopant and flux etc. is first prepared, which is fired at a comparatively higher temperature under controlled atmospheric conditions [Rotshchild 1956]. This method is quite useful for those materials for which techniques for preparing in other forms e.g. single crystals are not available. Even after single crystals of CdS, for example, were known; considerable interest still remained in preparing powders, which could be used to cover large areas.

(ii) Hydrothermal Synthesis Method:

In this method, a mixture of the ingredients are sealed in a quartz vial half filled with water and then fired at a comparatively lower temperature. The increased
temperature and pressure increase the solubility of the powder in water and during the subsequent slow cooling re-crystallization occurs [Kremheller and Levine 1957]. This method has been applied for the preparation of photoconducting powders with particle size less than 5 microns. Ratios of photocurrent to dark current as high as a million are reported, for powders prepared in this way.

(iii) Sintered Pellets:

Apart from these methods, powders can be compressed to form pellets, which are sintered at a comparatively high temperature under controlled atmosphere. Sintered pellets of CdS were prepared quite earlier by press moulding followed by sintering at 450°C for about 10 hours [Yoshimatsu et al 1955]. Also, Amalnerkar et al (1987) reported the preparation of sintered pellets of photoconducting CdS:Cu,Cl. Sintered pellets of PS were described by Putley (1952), who compressed the powder into blocks and then sintered at 1100 K for several hours in an atmosphere of H₂S.

3.1.2 Crystals

Single crystals have been prepared mainly by either the elemental constituent’s reaction or by sublimation of the compound followed by recrystallization. Miller and Bachman (1958) prepared single crystals of CdS by directing beams of evaporated Cd and S on to a common substrate in vacuum. Sublimation method was followed by Hollander (1957). Other methods used for the growth of single crystal are pulling from the melt [Medcalf and Fahring 1958], growth from solutions [Pankove 1954] and melting technique [Keck and Goley 1953]. Sasaki and Takahashi (1985) prepared CdS crystals at high temperature and pressure in the electrical furnace.
3.1.3 Thin films

Photoconducting materials can be prepared in the form of thin films. There are different methods for the deposition of thin films and are broadly classified under the following three techniques:

(i) Physical Vapour Deposition Methods

(ii) Chemical Deposition Methods

(iii) Sputtering Methods

(i) Physical Vapour Deposition Methods

In such techniques, creation of materials to be deposited involves a physical process. The different physical processes are described below:

(A) Thermal Evaporation:

Thin film deposition by thermal evaporation is simple and convenient and is thus one of the most widely used techniques. The solid materials in this method are heated to a very high temperature and the vapours are condensed on a cooler substrate and this yields thin solid films. By using this method, different metals, semiconductors and dielectrics can be evaporated on different substrates. Evaporation has also been a widely used technique in the preparation of photoconducting layers of PbS type materials. Such layers are usually prepared right in the complete envelope within which they are to be used as infrared detecting photocells. Sufficient material to produce a layer of about 1 micron thickness is placed on the container, which is then evacuated. The container is heated to about 600°C to evaporate the material, while the outer wall of the container opposite the electrode surface is cooled so that the material condenses there as a mirror like layer; then this layer in turn evaporates onto the cooled electrode surface [Bube 1967]. On heating a
material in vacuum, the evaporation rate is given by the well known Langmuir-Dushman expression and due to vacuum, the mean free path between collisions of vapour atoms to gas atoms becomes large enough so that the vapour beam arrives at the substrate unscattered [Chopra 1969].

The evaporation in this method may be achieved directly or indirectly by variety of physical methods described below:

(a) Resistive Heating:

This method consists of heating the material with a resistively heated filament or boat generally made of refractory metals such as W, Mo, Ta and Nb, with or without ceramic coatings. Crucibles of quartz, graphite, alumina, beryllia and zirconia are used with indirect heating. The choice of the support material is primarily determined by the evaporation temperature and resistance to alloying and/or chemical reaction with the evaporant.

(b) Sublimation:

If a sufficiently high vapour pressure is applied on a material before it’s melting, it sublimates and the condensed vapour form a thin film [Hüijer 1963]. Since the rates of sublimation for most of the materials are small, this method does not find wide applications. However, a useful application has been obtained in sublimation of resistively heated Nichrome wires [Chopra 1969].

(c) Arc Evaporation:

Sufficiently high temperatures are generated to evaporate materials by striking an arc between two electrodes of conducting materials [Karminsky 1965]. This method is widely used for evaporation of carbon for electron microscope specimens, employing a
standard d.c. arc-welding generator connected to the electrodes with a capacitor across the electrodes.

(d) Laser Evaporation:

The heat produced due to enormous intensity of laser is used to vaporize materials. The laser evaporation is done by keeping the laser source outside the vacuum system and the beam on to the surface of a material to be evaporated [Smith and Turner 1965, Schwarz and Tourtellotty 1966] although evaporation takes place at the surface only, because of the small (~100 Å) penetration depth of laser. Degassing and explosion of the specimen can be minimized by using the material in a fine powder form (~10 μm).

(e) Flash Evaporation:

A rapid evaporation of multi-component alloy or compound, which tends to distil fractionally, may be obtained by continuously dropping fine particles of the material on to a hot surface so that numerous discrete evaporations occur [Himes et al 1962, Richards 1966]. To avoid non-stoichiometric film deposition of intermetallic compounds, in which one of the components evaporates faster than the others, this technique is useful [Beam and Takahasi 1964].

(f) Exploding Wire Technique:

This technique consists of exploding a wire by a sudden resistive heating of the wire with a transient high current density approaching $10^6$ A/cm$^2$ [Conn 1950]. This is obtained by discharging a bank of condensers (~10 to 100 μF), charged to a voltage ~1 to 10 kV through a metallic wire.
(g) RF Heating:

The radio frequency (RF) or induction heating may be supplied to the evaporant directly or indirectly from the crucible material. To eliminate the possibility of contamination of the film by the support material by suitable arrangement of the RF coils, the induction-heated material can be levitated [Roth et al. 1962, Tanui et al. 1963]. CdS layers were obtained by vacuum evaporation to yield solar cells [Burton and Hench 1976]. Crystalline structure and the conductivity of the vacuum deposited CdS films on the quartz substrates were recently reported by Magafas et al. (1989). The polycrystalline Zn$_x$Cd$_{1-x}$S films prepared by vacuum deposition [Burton and Hench 1976, Chopra and Banerjee 1978] were used for hetero-junction solar cells.

(h) Electron Beam Heating:

In this method, the heat generated due to conversion of kinetic energy of electron when the electron beam is focused on the material which may be as high as 3000°C is used to evaporate it and hence refractory metals such as W, Mo, Ta can be used to evaporate by this method. Since temperature is high only at the focused spot, rest of the material remains cool, there occurs lesser interaction between the material and the support and thereby contamination is reduced. In this process, extremely high rates of evaporation can be achieved by applying very high input power. By this process, high melting point materials can also be evaporated at high rates [Chopra and Randlett 1966]. Films of Zn$_x$Cd$_{1-x}$S ternary alloys were prepared by evaporating a homogeneous mixture of ZnS and CdS powder with different alloy compositions $x$ by Mounir and Asmy (1988). Thin films of CdSe on glass substrates were prepared by Kissinger et al. (2007), using this method. This is the best method for the deposition of metal alloys, refractory...
metals etc. at a high rate and is now routinely used for the production of metal film resistors and others. Multi electron beam sources are also used for special applications.

(B) Molecular Beam Epitaxy (MBE):

The deposition of single crystal film by the condensation of one or more beams of atoms from Knudsen sources under ultra high vacuum (UHV) condition is called Molecular Beam Epitaxy [Mathews 1975, Kakati 1981] or MBE. Royer L. (1832) introduced the term epitaxy (arrangement on) to denote the phenomenon of the orientated growth of one substance on the crystal surface of a foreign substance. MBE makes it possible to deposit epitaxial films of compound semiconductors having precisely controlled properties. The growth temperature in MBE is low, which minimizes the unwanted thermal effects like diffusion. The growth rate is small, which makes it possible to deposit films with precise thickness control. MBE technique has been used to deposit multilayer structures of compound semiconductors to form quantum well superstructures, hetero-structures and graded composition structures. Bosacchi et al (1983) reported the growth of CdS and InP substrate using MBE technique. The results suggested that MBE is a suitable technique for preparing high efficiency CdS solar cells.

(C) Activated Reactive Evaporation (ARE):

When the evaporated material is transported through a reactive gas plasma, the deposition technique is called ARE [Powell et al 1966]. The technique has been mainly used to deposit highly adherent films of oxides and carbides. This technique may be divided into two categories: (i) biased ARE and (ii) enhanced ARE. In the former case, the substrate is biased, normally negative to attract the positive ions, and a positively biased electrode between the source and the substrate is used to create the plasma. In the
later case, the plasma is enhanced by accelerated electrodes emitted from a tungsten filament under electric field perpendicular to the vapour beam.

(D) Ion Plating:

In this technique, the substrate and the film are exposed to a flux of high energy ions during the deposition [Mattox 1967]. The evaporation of material is done by resistive heating or electron beam evaporation. Plasma is created in the working gas either by keeping the substrate at a high negative potential or by electron from a hot filament accelerated by an anode. Ion plating has been done to get better film adhesion especially for an incompatible substrate film contamination. This technique is used to deposit films for lubrication wear and corrosion resistance.

(II) Chemical Deposition Methods:

Chemical deposition techniques are the most important methods for the growth of thin films. These techniques enable coating thickness to be varied from Å to fraction of mm, in a well-controlled fashion and have widespread application of major technical and commercial values [Chopra 1969]. The various chemical deposition techniques are given below:

(A) Chemical Vapour Deposition:

When a volatile compound of the material is to be deposited is vapourized and the vapours thermally decomposed or reacted with other gases, vapours or liquids at the substrate to yield non-volatile reaction products which deposit atomistically on the substrate, the process is called chemical vapour deposition [Powell et al 1966]. Since a large variety of the chemical reactions are available, Chemical vapour deposition is a versatile and flexible technique in producing deposits of pure metals, semiconductors and
insulators. A very significant application of chemical vapour deposition process is the preparation of single crystal metal oxides, notably the ferrites, garnets, sapphire or MgO etc. Using this technique, Razykov (1985) prepared polycrystalline ZnCd$_x$S films used for heterojunction solar cells. Vengateshwar et al (1987) reported the growth of CdS thin film by open tube chemical vapour transport method. Although no electric currents or fields are required in a chemical vapour deposition process, the application of a transverse electric field to substrate during deposition is known to increase the growth rate of Si, Ge and GaAs [Tarui et al 1963; Chopra 1969]. Sharply pointed pyramidal CdSe nanostructures were grown on Si substrates by metal-organic chemical vapour deposition using Au as a catalyst by Shan et al (2005).

(B) Spray Pyrolysis:

The thermal decomposition of compounds to yield a deposit of the stable residue is called pyrolysis. Organometallic compounds decompose at lower temperatures (< 600° C) whereas metal halides particularly the iodides decompose above 600° C to yield metallic deposits. In this method, the substrate is kept at an elevated temperature and the solution containing salts of the constituent atoms of the compound is sprayed over it. Krunks et al (1986) reported the formation of CdS films by spray pyrolysis of neutral aqueous solution of CdCl$_2$ and SC(NH$_2$)$_2$. Using this technique, films of CdS were grown by Gupta (1999).

(C) Electrodeposition:

(a) Electrolytic Deposition:

It is one of the widely used techniques. According to the law of electrolysis, the
weight of the material deposited is proportional to the amount of electricity passed. 1 gram equivalent of the material is deposited by 96490 Coulombs of electricity. The metallic ions in the electrolyte migrate towards the cathode under the influence of the applied electric field, which can be as high as $10^7$ V/cm. In this method, a suitable electrolyte is required through which current is passed between the two electrodes. The deposition rate is proportional to the electrolysis time and the current density (Chopra 1969). Anuradha and Pandian (1990) prepared CdS thin films by electro-deposition technique. Cd$_{1-x}$P$_x$Te thin films were cathodically deposited by Singh Santosh (1999).

This technique has been successfully employed for deposition of thin films of elemental, binary and ternary semiconductors [Bhattacharya and Rajeshwar 1984, Chandra and Sahu 1984].

(b) Electroless Deposition:

Electrolytic action may be achieved without an external potential source by a chemical reduction process such as that used in the technique of silvering glass dewars [Lowenheim 1963] for depositing Ni, Co and Pb films by reduction of their chlorides by sodium hypophosphite. For non-metallic surfaces, it may be necessary to use a sensitizer such as 0.1 percent stannous chloride. The rate of film growth by this method depends greatly on the reaction temperature and is generally difficult to control [Chopra 1969].

(c) Anodic Deposition:

This is an electrolytic process, in which the metal is made the anode in a suitable electrolyte. A large number of metals tend to force a protective oxide film of limited thickness when exposed to oxygen. By anodic polarization of these metals in a suitable aqueous solution (which does not dissolve the oxide), a protective high resistance film
can be grown. The anodization process involves migration of oxygen ions and metal ions or both, depending on the material, through the existing oxide film. The rate of growth of an anodic film depends on the current density and the temperature of the electrolyte. A simple arrangement consists of an electrolytic cell with a cathode of the same material as the anode or of platinum. By anodic polarization of the metals, a protective high resistance film can be grown [Young 1961].

(D) Solution Growth:

The growth of films on either metallic or non-metallic substrates by dipping them in appropriate solutions containing metal salts without the application of electric field is one of the cheapest and simplest methods. Compounds of films such as sulphides and selenides of Pb, Zn, Hg and Cd and their alloys were deposited by this technique (Moss 1955). According to Pavaskar et al (1977) CdS films of right stoichiometry, good adhesion and uniform thickness over a large area can be obtained by chemical bath deposition method. Chemical bath deposition (CBD) method was used by different workers [Büger et al 1971, Chopra and Das 1983, Pentia et al 2001] for the deposition of PbS films. PbS films were also deposited on other semiconducting materials e.g. Si, Ge or InP [Gudaev et al 1991, Isshiki et al 1990] on ferro-electric ceramics (Pintilie et al 1995) or on dielectrics (Pintile et al 2000). Nair et al (1989) prepared thin films of PbS, Cu,S and PbS-Cu,S on glass substrates by chemical deposition method. Chandra and Sahu (1984) used such films in PEC solar cells. Karanjai and Dasgupta (1988) prepared (Cd-Zn)S films by dip techniques. Nair et al (1989) prepared thin films of PbS, Cu,S and PbS-Cu,S on glass substrates by chemical deposition method (by solar radiations). Bari et al (2006) prepared thin films of copper indium diselenide by CBD
technique on glass substrates. It is known that the chemical deposition of thin film starts with a nucleation phase (also known as incubation or induction period) followed by a growth phase in which the thickness of the film steadily increases and culminating in a terminal phase at which the thickness of the film steadily increases (referred to as the terminal thickness) because the bath becomes depleted of the constituent ions for the film formation. The nucleation phase is required for the formation of critical nuclei on place through metal hydroxide ions present in the aqueous alkaline/ammoniacal bath [Nair et al 1989].

(E) Screen Printing:

In screen-printing, the paste containing the desired material is screen printed onto a suitable substrate by conventional methods. Chlorine and copper doped polycrystalline CdS films were prepared by coating slurry on a glass substrate by Mounir and Asmy (1988). Ramprakash et al (1988) also prepared CdS films by this technique. Padam et al (1988) reported physical and electrical properties of thick films of \((\text{Cd}_{1-x}\text{Zn}_x)\)S. In the composition range from pure CdS to pure ZnS and sintered at 800°C.

(III) Sputtering Techniques:

The ejection of atoms from the surface of a material (the target) by bombardment with energetic particles is called “sputtering”. The ejected or sputtered atoms can be condensed on a substrate to form a thin film. There are various types of sputtering techniques as given below:

(A) Cathodic Sputtering:

The ejection of atoms from the cathode surface by impinging energetic positive ions of noble gases such as helium, argon, neon, krypton at a reduced pressure under a
high d.c. voltage gives rise to the sputtering phenomenon. The deposition of metal films by sputtering from a cathode by the glow discharge method was first observed by Grove in 1852. The practical application of the sputtering process to thin film deposition and the properties of sputtered films has been reviewed by several workers [Holland 1956, Wolsky 1963 and Maissel 1966]. The sputtering yield, defined as the average number of atoms ejected from the target per incident ion, increases with increasing energy of ions and their mass [Wehner in 1957; Almen and Bruce 1961] of the bombarding ions and with the decrease of angle of incidence to the target. The sputtering is also accompanied by the emission of secondary electrons (γ-electrons) from the cathode surface. Auger transition also takes place. The sputtered atoms are mostly neutral i.e. atomic in nature, about 1% may be in the ionized state. Part of the sputtered material may form polyatomic species and complexes but their relative abundance will be quite negligible compared to the number of neutral atoms.

(B) Radio Frequency Sputtering:

Enhanced ionization can be achieved in radio frequency field so that sputtering can be done at pressure lower than that of the ordinary glow discharge. There will be ionization of gases, with a low frequency a.c. field between two electrodes of a discharge tube, since both the electrodes will have alternate polarities. With increasing frequencies from 100 KHz to a few MHz there will be a sustained glow discharge due to the ionization of gases by the oscillating electrons of high frequency field [Maissel 1966]. This technique is particularly useful for the deposition of dielectric material. Metals can also be radio frequency sputtered [Goswami 1996].
(C) Ion-beam Sputtering:

By producing ions in a high pressure chamber and then extracting them into a differentially pumped vacuum chamber through suitable apertures with the help of suitable electron and ion optics, a beam of ions may be obtained for sputtering in vacuum. Chopra and Randlett (1966) designed an ion-beam source capable of yielding currents of ~500mA for a beam size of ~1 cm². The argon ions produced by them are extracted into a vacuum chamber through apertures by confining the plasma in the narrow aperture by means of suitable magnetic and electric fields. The rate of sputtering is approximately proportional to ion current for a constant accelerating voltage and therefore may be conveniently controlled [Chopra 1969].

(D) Mangetron Sputtering:

The ionizing efficiency may be increased very conveniently by increasing the path length of the ionizing electrons, for example by transverse magnetic field normal to the electric field. To obtain uniform deposition on a substrate, cylindrical cathode and a magnetic field parallel to the axis may be used and more uniform deposit can be obtained by placing the substrate inside the hollow cathode. In this method, the substrate used are glass or dye polyester [Ritchie and Wilfred 1987]. Two types of magnetron sputtering systems are widely used; (i) cylindrical type and (ii) planar type. (Zn₀.₁₅-Cd₀.₈₅)S films prepared by RF sputtering in an Ar-H₂ atmosphere were reported by Romeo et al (1988). Such cells were used in high efficiency solar cells. Abdul Ghafor (1990) reported the optical properties of (Cd₁₋ₓZnₓ)S by preparing films by sputtering techniques. The thickness of the film deposited at 50°C was around 1-micrometer. They showed the
possibility of using such films as anti-reflection coating when deposited on the surface of silicon solar cells.

3.1.4 OTHER STRUCTURES

Many photoconductors have been prepared in junction forms with controlled dark conductivity and photosensitivity by incorporation of suitable impurities [Weiser 1958]. Materials having p-n and n-p-n structures [Bube 1967] and heterojunctions of Cu$_2$S-CdS [Lindquist and Bube 1972, Fahrenbruch et al 1974] etc. also showed good photoconductivity. Farrell et al (1988) suggested mechanism by which light interacts with surface species during growth using MBE for making p-n junction in II-VI materials.

3.1.5 Present Method of Preparation

The present technique of preparation of photoconductors is deposition of film by the method of chemical bath deposition. The deposition of films can be explained as follows:

The CdS and Cd(S-Se) films were deposited on the surface of commercial quality microscope glass slides of dimensions 24 mm x 75 mm, which were first cleaned with dil. HCl, acetone and double distilled water. The films were prepared by vertically dipping the cleaned glass slides in a mixture of solution of 1M cadmium acetate, appropriate ratio of thiourea and sodium selene-sulphate [Na$_2$SeSO$_3$] solution prepared by heating elemental selenium (99.9% pure) in aqueous solution of sodium sulphite [Na$_2$SO$_3$] at 90°C for 5 hrs. triethanolamine (TEA), solution of 0.01M cadmium chloride and 30% aqueous ammonia. All the chemicals used were of AR grade.
The deposition were done in a constant temperature water bath (Tempo) at about 60° C. All the solutions were prepared in double distilled water. The glass slides were kept vertical against the wall of a 50 ml beaker containing the mixture of the above solutions. For preparing doped films, calculated proportion / s of 0.01M solution of samarium / dysprosium nitrate (99.9 %) were mixed to the original mixture and then the depositions were made. Triethanolamine and ammonia solution were used to adjust pH of the reaction mixture and to increase film adherence. To obtain good quality films time, temperature of deposition and pH of the solution were optimized. The optimum time and pH were observed to be 1 hr and 11.2 respectively. The arrangement for preparing the thin film is shown in fig.-3.1(a) and (b). No stirring was done during the deposition. After deposition, the films were cleaned by flushing with distilled water and then dried by keeping the samples in open atmosphere at room temperature.

Fig.-3.1(a) Experimental Arrangement for preparing Films
The mechanism of deposition of Cd(S-Se) films is based on the slow release of Cd\(^{2+}\) and S\(^{2-}\) ions in aqueous basic solution and subsequent condensation of these ions on the substrates vertically mounted in the solution. The slow release of Cd\(^{2+}\) ions is achieved by the dissociation equilibrium of a complex species of cadmium Cd(TEA\(^{2+}\)) \[\text{Ezema and Osuji 2007}\].

\[
([\text{Cd(TEA)}]^{2+} \leftrightarrow \text{Cd}^{2+} + \text{TEA}) \quad \text{----- (3.1)}
\]

The S\(^{2-}\) ions are provided by the dissociation of thiourea \([\text{SC(NH}_2\text{)}_2]\) in the ammoniacal medium.

\[
\text{SC(NH}_2\text{)}_2 + \text{OH}^- \rightarrow \text{CH}_2\text{N}_2 + \text{H}_2\text{O} + \text{HS}^- \quad \text{----- (3.2)}
\]

\[
\text{HS}^- + \text{OH}^- \leftrightarrow \text{S}^{2-} + \text{H}_2\text{O} \quad \text{----- (3.3)}
\]

The hydrolyses of sodium seleno-sulphate (Na\(_2\)SeSO\(_3\)) in the solution to give Se\(^{2-}\) ions is according to the chemical reaction:

\[
\text{Na}_2\text{SeSO}_3 + \text{OH}^- \leftrightarrow \text{Na}_2\text{SO}_4 + \text{HSe}^- \quad \text{----- (3.4)}
\]
Similarly, the hydrolysis of ammonia in water to give OH\(^-\) ion is according to the equation:

\[ HSe^- + OH^- \leftrightarrow H_2O + Se^2^- \]  \hspace{1cm} (3.5)

When the ammonia is added to the Cd\(^{2+}\) salt solution, Cd(OH)\(_2\) starts precipitating, when the solubility-product (SP) of Cd(OH)\(_2\) is exceeded.

\[ Cd^{2+} + 2 OH^- \leftrightarrow Cd(OH)_2 \]  \hspace{1cm} (3.7)

The Cd(OH)\(_2\) precipitate dissolves in excess ammonia solution to form the complex Cadmium tetra-amine ions \([Cd(NH_3)_4]^{2+}\).

\[ Cd^{2+} + 4 NH_3 \leftrightarrow [Cd(NH_3)_4]^{2+} \]  \hspace{1cm} (3.8)

Finally, the deposition of Cd(S-Se) thin film occurs, when the ionic-product of Cd\(^{2+}\) and S\(^2-\) or Cd\(^{2+}\) and Se\(^2-\) ions in the solutions controls the rate of precipitation and hence the rate of film formation [Kale and Lokhande 2004].

\[ [Cd(NH_3)_4]^{2+} + S^{2-} + Se^{2-} \leftrightarrow Cd(S-Se) + 4 NH_3 \]  \hspace{1cm} (3.9)

The growth mechanism of thin films using chemical bath deposition (CBD) method can take place either in the bulk of the solution (homogeneous precipitation process) or at the substrate surface (heterogeneous process). It can be considered as "cluster by cluster" growth, leading to the particulate films. The lattice is a growth mechanism involving the reaction of atomic species at the surface, it corresponds to an atom by atom process, also called "ion by ion" process [Kaur et al 1980].

The Cd(S\(_{0.95}\)-Se\(_{0.05}\)) films (used for PC rise and decay studies) were yellowish in colour and the Cd(S\(_{0.7}\)-Se\(_{0.3}\)) films (used for PL studies) were dark brownish, as shown in fig.-3.2 (a) and (b).
Annealing of the films was done in air at a temperature of 350°C for 3 minutes.

For annealing, a tubular furnace fabricated in the department was used. The design of this furnace is shown in fig.-3.3. Windings of kanthal heating wire were done on the external surface of a silica tube. Layers of asbestous powder were placed on this winding so as to avoid the radiation-loss. The whole apparatus was kept in a rectangular iron box. The tube was closed from one side and kept open from the other side so that the glass slide to be annealed could be placed inside the furnace. Proper temperature were maintained by controlling the current flowing through the coils with the help of a variac. The temperatures were measured with the help of an accurate thermometer.
3.2 Thickness-Measurement

Thickness is one of the significant film parameters. It can be measured either by monitoring the rate of deposition or after the deposition by various other methods. Different methods normally used for the determination of thickness are described below:

3.2.1 Electrical Methods:

(A) Film resistance:

This simple method is applicable to metallic and low resistivity semiconductor films. It depends on the fact that the resistance is related to the film thickness and the mean free path of the charge carriers and thus measurement of resistance; and can lead to determination of film thickness. Resistance of the film can be measured by making the film one arm of a d.c. or a.c. Wheatstone bridge. For a given value of the ratio arms of the bridge, the film-resistance is proportional to the variable resistance, which can be measured by automatically recording the potential across it [Benett and Flangan 1960]. Electrical resistivity and Hall coefficients of metal and semiconductor film may be measured. Using the reciprocity theorem, these values can be determined and the film-thickness can then be determined [Leonard and Ramey 1964].

(B) Capacitance Monitors:

The thickness of the film can also be measured by monitoring the electrical capacitance of the film using capacitor configuration [Keister and Scrapple 1962]. These workers constructed a capacitance monitor plate by depositing Al-films and then photoetching the comb pattern. Riddle (1962) measured the rate of evaporation by measuring the changes in the dielectric constant resulting from the presence of the vapour of the evaporant.
(C) Ionization Monitoring:

By ionizing the vapour from the evaporant and measuring the resultant ion current, the evaporation rate can be monitored and controlled via a feedback servomechanism. This method, used for detection of molecular beams, was first adapted to thin films by Metzer (1943) and has since been utilized by a number of workers. The ion current is proportional to the total number of vapour atoms and their ionization monitors can be operated in ultrahigh vacuum conditions and at high temperatures.

3.2.2 Mechanical Method (Stylus)

Variation in the movements of a mechanical stylus can be amplified electronically so that step heights and the surface irregularities of 10Å can be measured. This method is quite popular for measuring film thickness and surface irregularities [Silver and Chow 1965]. The stylus in this case consists of a diamond with a rounded (~0.7 to 1.3 μ-diameter) or four sided pyramid tip fastened to a lever arm. The arm is delicately balanced so that the load on the stylus is very small. The vertical movement of the stylus is detected with a transducer, amplified $10^5$ to $10^6$ times, and then fed with a recorder.

3.2.3 Radiation-Absorption and Radiation-emission Method

As the optical absorption of light, X-rays, α-rays and β-rays depend on the thickness of the film; this method can be used for the determination of thickness of the film [Mase et al 1967]. The optical absorption (or density) depends exponentially on the film thickness for the continuous films. The absorption of discontinuous films is strongly influenced by the granular nature of the films, but it may still be used for relative measurement of the average film thickness. The optical absorption can also be used for monitoring during deposition by glow discharge sputtering. Absorption or scattering of
X-rays, α-rays and β-rays emitted from radioactive isotopes have been employed for the measurement of thickness and from less than 100 Å to about 1 mm may be measured using α and β-ray absorption [Friedman and Briks 1946, Davisson 1957, Cameron 1960, Schmacher and Mitra 1962]. The maximum thickness is limited to several thousand angstroms for 100 KeV electrons. It is a particularly useful technique for thin insulator films. When radiations are incident on a surface, some scattering takes place. The back scattering of β-rays depends on atomic number, density and thickness of the scattering material, and its measurement is, therefore, used for the determination of the film density and thickness. A system for measuring the scattered electrons (and hence the film thickness) in the Debye-Scherrer cone has been described by Behrens (1961). X-ray emission also known as x-ray fluorescence, is a nondestructive technique for determination of mass of the material component and hence the film thickness and the chemical composition. One technique is to excite them in the substrate using white X-ray radiation or an energetic electron beam and measure their attenuation in the film material. Cockett and Davis (1963) showed that film excitation is more accurate method for the measurement of thickness up to about a quarter of the electron range, while the substrate-excitation method is better for thicker films.

3.2.4 Microbalance Monitors

(A) Microbalances:

These monitors are termed as “gravimetric” or “momentum” type depending on whether they measure the “weight” or “momentum” of the impinging vapour, respectively. The first method is the oldest and most convenient method for determination of film thickness. Balances, which employ null-balance principles using
mechanical, optical, electromagnetic or electrostatic detection methods in different types of balances such as pivotal, torsion, fiber, quartz or tungsten helical, spiral and magnetic suspension, have found application as monitors. Vacuum microbalances are also used since 1960. The detection sensitivities of various balances ranges from 1 to $10^{-2}$ μg. Campbell and Blackburn (1960) used microbalance monitors having moving coil current meters. A simple torsion pendulum was used to measure the momentum transfer rate. The resulting momentum exchange caused a rotation about the axis of the cylinder. The rotation clearly depends on the number, mass and velocity of the impinging vapour [Chopra 1969].

(B) Quartz Crystal Monitor:

In this method for the measurement of thickness of the film, a sensitive and rugged microbalance is used on measuring changes in resonant frequency of a quartz-crystal oscillator with mass loading when operated in a particular mode of vibration. A quartz-crystal monitor for monitoring and controlling the rates of both deposition and evaporation of metals, non-metals and multi-component films is the most important monitor for thin film technology [Warner and Stockbridge 1963]. The monitor utilizes the thickness shear mode of piezoelectric quartz crystal. Here the major crystal surfaces are anti-nodal and mass added on either one or both sides shift the resonance frequency irrespective of the thickness, density, elastic constants or stiffness of the added material [Chopra 1969].

3.2.5 Optical Interference Methods

If the optical constants are known, the thickness of the film can be calculated. Among these methods are the photometric and spectro-photometric techniques, which are
based on the optical interference phenomenon and find widespread applications for measurements and control of multi-layer dielectric and semiconductor films.

(a) Photometric Method:

If a transparent or slightly absorbing film is deposited on a transparent substrate of different refractive index, the optical reflectance and transmittance behaviour of the film-substrate combination shows an oscillatory behaviour with increasing film thickness, because of interference effects. Reflectance is reduced or enhanced depending on the relative values of the indices of the film and substrate material. Lindsberg and Irland (1955) used two photocells in series. One cell monitored the reflected intensity from the sample and the other was illuminated from a variable intensity light source to provide a bucking or nulling signal so that only the oscillatory part is obtained and amplified. This procedure allowed monitoring up to 15 layers.

(b) Spectrophotometric Method:

When light is incident at an angle $\theta$ from a medium of index $n_0$ onto a film of Index $n_1$ and thickness $t$, deposited onto a substrate of index $n_2$, with $n_1$ lying between $n_0$ and $n_2$, the reflected light will show an interference maximum for a wavelength $\lambda$ when the path difference $2n_1t \cos \theta$ between the successive beams reflected at each surface is equal to $m\lambda$, where $m$ is an integer if $n_1 > n_0, n_2$. The reflected intensity will show a minimum (dark band results) when $2n_1t \cos \theta = m\lambda$ and a maximum if $2n_1t \cos \theta = (m - 1)\lambda/2$. An interference maximum will produce a characteristic hue of the film when white light is used. The reflected light will show maxima for various wavelengths for which the interference condition is satisfied. A spectrophotometer may be employed to measure the transmitted or reflected intensity as a function of the wavelength and then records
positions of maxima and minima. Thus, thickness 't' can be determined provided the
refractive index does not vary rapidly. In this method, a double beam recording
measurement of epitaxial semiconductor films deposited on different substrates are used
for thickness measurement.

(c) Interference Fringes:

Film thickness can also be measured accurately from interference fringes using
multiple beam interferometries and from the fringes of equal chromatic order techniques.
Weiser (1887) was the first to use interference method for the measurement of the
thickness of films. In the former case, two reflecting surfaces are brought in close
proximity such that a small wedge with a small air gap in between them is formed. If a
monochromatic light is now made incident on them at normal incidence, then an
interference of light due to interactions of multiple reflected beams in air gap will take
place resulting in a series of fringes [Fizeau] which can be observed in the back
reflected light. The distance between the fringes or lines depends on the air gap as well as
on the wavelength of the monochromatic light. This principle is adopted and suitably
modified for the multiple beam interferometric method for the measurement of thickness.
If instead of the air wedge, two parallel plates illuminated with white light are used,
fringes will occur at wavelengths for which \( t/\lambda \) is constant so that the resulting spectrum
is banded. Heavily silvered plates are again necessary to obtain fine fringes. In reflection,
fringes appear dark on bright background. In transmission, the complementary pattern is
seen. If one of the plates is covered by a film, a displacement \( \Delta \lambda \) is seen in the \( m^{th} \) order
fringe from which film thickness can be calculated by using the formula

\[
t = (m/2) \Delta \lambda
\]
The sharpness of fringes depends on the reflectivity of the metal coating, the spread of the incident beam and air-gap, etc. Thickness down to about 75 Å can be measured by this method [Goswami 1996].

3.2.6 Present Method of Thickness Measurement

In the present study, parallel beam of sodium-light is made incident on the film clamped between two glass plates, as shown in fig.-3.4 (a). Due to interference, straight fringes with bend at the edge of the film boundary are formed, as shown in fig.-3.4 (b).

The thickness of the film is determined by using the formula [Goswami 1966]:

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

where 'b' is displacement of fringes, 'a' is distance between two successive fringes (fringe-width) and 'λ' is the wavelength of light used.

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Fig.- 3.4 (a) Experimental arrangement for thickness-measurement of different Cd(S-Se) films
It is observed that the film thickness increases with increase in dipping time. The behaviour of increase in thickness of Cd(S$_{0.95}$-Se$_{0.05}$) film with dipping time is shown in fig.- 3.5. The highest photoresponse was found for a dipping time of 60 minutes and therefore for the PC and PL studies, included in the thesis, all the films were prepared at 60 min. dipping time. The thickness of the different Cd(S$_{0.95}$-Se$_{0.05}$) films were found to lie in the range of 0.4694 - 0.4837 $\mu$m for 60 min. dipping time.

Fig.- 3.5 Variation of thickness with dipping time for the Cd(S$_{0.95}$-Se$_{0.05}$) film
3.3.1 Rise and Decay Studies

For preparing photoconducting cell in the thin films, coplanar silver paint electrode of 2 mm width and 24 mm length were applied on the surface of the film at a separation of 2 mm, as shown in fig.- 3.6.

![Photoconductivity Cell](image)

A set up described in fig.-3.7 was used for the photoconductivity rise and decay studies of the films. A 100 Watt commercial bulb was used as the excitation source and a regulated powder supply (Unitec) for biasing purpose in case of films. The corresponding photocurrent in the lower range (1 nA to 100 µA) was recorded by a nanometer (NM122 from M/S Scientific equipments, Roorkee, sensitivity 1 nA) and the current in the higher range (above 100 µA) was recorded by digital multimeter (HM 5013 from M/S Scientific equipments, Roorkee, sensitivity 1 nA). The dark current was recorded by digital pico-ammeter (DPM 111. from M/S Scientific equipments, Roorkee, sensitivity 0.001 nA).
3.3.2 Spectral studies

(i) Absorption Spectra

For recording absorption spectra, a Shimadzu (UV-VIS) PheraSpec 1700 Spectrophotometer, shown in fig.-3.9 (a) and (b) was used in the 300-700 nm wavelength range.
Fig.- 3.9 (a) Shimadzu (UV-VIS) PhermaSpec Spectrophotometer

Fig.-3.9 (b) Experimental Set up for recording Absorption Spectra
To facilitate the recording of optical absorption spectra, the films from one side of glass substrate were removed by cotton swabs dipped in concentrated HCl. For the absorption measurements, the beam was allowed to enter the film through the glass substrate and an uncoated identical glass substrate in the reference beam for compensation. From these studies, the absorption coefficients were calculated which were used in deriving the band-gap of the material prepared.

(ii) Photoluminescence Emission Spectra

A setup described in fig.- 3.8 was used for the PL emission spectral studies of the films. Such studies were performed by exciting the material with 365 nm Hg radiation from Hg lamp and Carl Zeiss interference filter and PL intensities corresponding to different wavelengths were recorded by using a prism monochromator and an RCA-6217 photomultiplier tube which was operated by a highly regulated power supply. The corresponding currents were recorded by using a polyflex galvanometer (10^6 A/mm).
Excitation Source (Hg)

Interference filter for 3650 Å

Film

Filter for cutting UV

Grating / Prism monochromator

RCA 6217 Photomultiplier tube

Polyflex galvanometer

Power supply

Voltage stabilizer

A.C. Mains

Fig. 3.8 Block diagram for PL emission spectral studies
3.3.3 Characterization Studies

Some of the important methods used for characterization of the thin films are described below:

(i) Bulk Structure

The X-ray diffraction (XRD) and TEM are the most widely used techniques for the determination of crystallographic structure of the bulk of the thin film. The XRD technique used for film with thickness greater than 1000 Å., gives a wide range of information such as lattice-constants, crystal structure, orientation defects and stresses in thin films. In TEM, when operated in diffracted mode, the diffracted intensities are much stronger compared to XRD and thus allows defect structures to be imaged in addition to obtaining diffraction patterns which give the lattice-constants, orientation and other crystallographic information.

(ii) Topography

The different methods/ instruments used for viewing the surface of the thin films are: The Stylus techniques, Optical Microscope, Scanning Electron Microscope (SEM) and Tunnel Electron Microscope (TEM).

SEM is the most widely used instrument for obtaining topographical features of a thin film. In SEM, a magnification of the order of $10^5$ can be obtained with a resolution of 30 Å. TEM is another method and in replica mode provides the best topographical resolution ~ 20 Å. In stylus techniques, a sharply pointed stylus is rested lightly on the surface and is traversed across it. The up and down movements of the stylus which correspond to the surface texture of the film is picked up by a transducer element.
amplified and fed to the recording device. The optical microscope can also be used for viewing the surface of the film; however, the spatial resolution is limited in this case.

(iii) Surface Structure

For many applications like catalysis, corrosion and work-function determination, the structure of the first few monolayers of the specimen is important criterion. Such surface sensitive structure analysis can be done by techniques like low Energy Electron diffraction / Field Emission Microscope / Field Ion Microscope / Atomic Probe / Field Ion Microscope and Reflection High Energy Electron Diffraction etc.

(iv) Chemical Analysis

Chemical analysis describes the various aspects including identification of various elements present, quantitative chemical Composition, Chemical States of the elements and distribution of each element across the thickness of the thin film as well as over the surface. Some of the methods/ instruments employed for chemical analysis are Electron Probe Micro-analyzer, Auger Electron Spectroscope, Scanning Auger Microscope, Electron Spectroscopy for Chemical Analysis, Ion Scattering Spectroscopy, Secondary Ion Mass Spectroscopy and Rutherford Back Scattering.

3.3.4 Present Methods of Characterization Studies

XRD and SEM methods were used to characterize the materials. The instruments used for XRD and SEM studies of the different films at IUC-DAE, Indore ( M.P. ) were Rigaku RU3HR X-ray diffractometer and JEOL ( JSM - 5600 ) scanning electron microscope respectively and are shown in fig. 3.10 and 3.11 respectively.
Fig. 3.10 - Rigaku RU3HR X-ray Diffractometer

Fig. 3.11 - JEOL (JSM - 5600) Scanning Electron Microscope

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