CHAPTER-III

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 photoconducting materials.
3.2 Thickness determination.
3.3 Measuring arrangements.

Now we will describe them one by one.

3.1 Preparation of Photoconducting Materials

Photoconductors can be prepared in different forms like powders, crystals and thin films etc. The different preparation 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, 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 molding 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 PbS were described by Putlay (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 zone melting techniques (Keck and Golay 1953). Sasaki et al. (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 Techniques

(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 surfaces is cooled so that the material condenses there as a mirror like layer; then this layer in turn evaporated onto the cooled electrode surfaces (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 collision 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 vapours form a thin film (Huijer 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 (Kikuchi 1965). This method, widely used for evaporation of carbon for electron microscope specimens, employs a standard dc 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 vapourize 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 & Turner 1965, Schwarz et al. 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 (~10μ).

(e) Flash Evaporation

A rapid evaporation of multicomponent 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 evaporation 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 Takahashi 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 10⁶ A/cm² (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, Turner et al. 1963, Audenhove 1965). CdS layers were obtained by vacuum evaporation to yield solar cells (Burton 1976). Crystalline structure and the conductivity of vacuum deposited CdS films on the quartz substrates were recently reported by Magafias et al. (1989). The polycrystalline ZnxCd1-xS films prepared by vacuum deposition (Burton and Hench 1976, Chopra et al. 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 the 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 ZnxCd1-xS ternary alloys were prepared by evaporating a homogeneous mixture of ZnS and CdS powder with different alloy composition ‘x’ by Mounir and El Asmy (1988). 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.
L.Royer (1836) introduced the term epitaxy (arrangement on) to denote the phenomenon of the oriented 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 super structures, hetero-structures and graded composition structures. Bosacchi et al. (1983) reported the growth of CdS and InP substrate using MBE technique. The results suggested the MBE is a suitable technology 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 electrons 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 1982). 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 used 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 angstroms to fractions of millimeters in a well-controlled fashion and have widespread applications 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 to be deposited is vapourized, and the vapour is 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 chemical reactions are available, CVD is a versatile and flexible technique in producing deposits of pure metals, semiconductors, and insulators. A very significant application of CVD processes is the preparation of single crystal metal oxides, notably the ferrites, garnets, sapphire, MgO etc. Using this technique Razykov (1985) prepared polycrystalline $Zn_x Cd_{1-x} S$ films used for heterojunction solar cells. Vengatesan et al. (1987) reported the growth of CdS thin films by open tube chemical vapor transport method. Although no electric currents or fields are required in a CVD 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).

(B) Spray Pyrolysis

The thermal decomposition of a compound to yield a deposit of the stable residue is called pyrolysis. Organometallic compounds decompose at low temperature (<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 soluble 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 solutions of CdCl₂ and SCN₂NH₂. 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 gm. equivalent of the material is deposited by 96490 Coulomb 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 10⁷ 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 et al. (1999) prepared CdS thin films by electro deposition technique. Cd₁ₓPbₓTe thin films were cathodically deposited by Singh et al. (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, Rosamilla and Miller 1986).

(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 et al., 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 Oxidation

This is an electrolytic process, in which the metal is made the anode in a suitable electrolyte. A large number of metals tend to form 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 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 method was used by different workers (Buger et al. 1971, Chopra & Das 1983, Pintia 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$_2$S and PbS-Cu$_2$S on glass substrates by chemical deposition method. Chandra et al. (1980) used such films in PEC solar cells. Call et al. (1980) prepared their films of ZnO. Karanjai and Dasgupta (1987) prepare (Cd-Zn)S films by dip techniques. Nair et al. (1989) prepared thin films of PbS, Cu$_2$S and PbS-Cu$_2$S on glass substrates by chemical deposition method (by solar radiations). 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 increase (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 Moon (1988). Ramprakash et al. also prepared CdS films by this technique. Padam et al. (1988) reported physical and electrical properties of thick films of (Cd$_{1-x}$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 dc 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 (Washner in 1957 and Almen et al. 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 ($\gamma$-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 (Maisel 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 (1967) 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) Magnetron 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. (Zn_{0.15-Cd_{0.85}}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 Guphor and Mazdi (1990) reported the optical
properties of (Cd$_{1-x}$Zn$_x$)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. Farrel 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 films by the method of chemical bath deposition. The deposition of films can be
explained as follows:

Different CdS, PbS and mixed base (Cd-Pb)S films at different
proportions of CdS PbS were prepared by chemical bath deposition method. The
films were deposited on the surface of commercial quality microscopic glass slides of
dimensions 24mm x 74mm. The films were also deposited on Al substrates of the
same size (i.e. 24mm x 74mm). For the deposition of the films the glass and the Al
substrates were washed with acetone and finally with double distilled water. The
films were prepared by vertically dipping the cleaned substrates in a mixture of
solutions of 1M cadmium acetate and 1M lead acetate (total 7ml.), 2 ml. of
triethanolamine (TEA), 25ml. of 30% aqueous ammonia and 7 ml. of 1M thiourea (all
A.R. grade). The pH of the mixture was about 11. The depositions were done in a
constant temperature water bath (Tempo) at 60°C. The temperature 60°C was
selected because it gave the highest ratio of photocurrent to dark current. All solutions
were prepared in double distilled water. The substrates (glass & aluminium) were
kept vertically against the wall of a 50ml. or 100ml. beaker containing the mixture of
above solutions. For preparing the doped films, calculated proportions of 0.1M solutions of NaF, nitrates of lanthanum and praseodymium (all A.R.grade, 99.9%) were mixed in the original mixture and then the depositions were made. The arrangement for preparing the thin film is shown in fig 3.1. Before dipping the substrates in the mixture, the solution was initially stirred with them and then rested against the walls of the beaker. No further stirring was done during the deposition. After the deposition, the films were cleaned by flushing with double distilled water and then dried by keeping the slides in open atmosphere at room temperature. Annealing of the films (prepared on glass substrates) was done in air at a temperature of 400°C for different times. For annealing a tubular furnace fabricated in the department was used. The design of this furnace is shown in fig 3.2. Windings of kanthal heating wire were made on the external surface of a silica tube. To avoid radiation loss, the windings of the wire were covered with asbestos powders. 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 temperatures were maintained by controlling the current flowing through the coils with the help of a variac. The temperature was measured with the help of an accurate thermometer.

The mechanism of deposition of (Cd-Pb)S films is similar to that of CdS. Deposition of CdS is based on the slow release of Cd\(^{2+}\) and S\(^{-}\) ions in an aqueous alkaline bath and subsequent condensation of these ions on the substrates suitably mounted in the bath. The slow release of Cd\(^{2+}\) ions is achieved by dissociation of a complex species of cadmium Cd (TEA)\(^{2+}\). The availability of Cd\(^{2+}\) ions is governed by the following dissociation equilibrium

\[
[(\text{Cd})\text{TEA}]^{2+} \rightleftharpoons \text{Cd}^{2+} + \text{TEA} \quad \ldots \quad (3.1)
\]

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

\[
[\text{SC(NH}_2)\text{)] + \text{OH}^{-} \rightarrow \text{CH}_2\text{N}_2 + \text{H}_2\text{O} + \text{SH}^{-} \quad \ldots \quad (3.2)
\]
FIG.- 3.1 THE WATER-BATH

FIGURE-3.2 THE TUBULAR SILICA FURNACE FOR ANNEALING.
\[ \text{SH} + \text{OH} \rightarrow \text{S}^- + \text{H}_2\text{O} \quad \ldots (3.3) \]

Since the solubility of CdS is low \(1.4 \times 10^{-29}\) (C.R.C.-1985), even very low concentrations of \(\text{Cd}^{++}\) and \(\text{S}^-\) ions released according to equations (3.1, 3.2 & 3.3) are sufficient to yield the solid phase.

### 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 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 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 Scapple, 1962). These workers constructed a capacitance monitor plate by depositing Al films and then photo etching 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 Hasse (1957) 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 10 Å 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 (~.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-ray & β-rays depends 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 100Å to about 1mm may be measured using α and β-ray absorption (Friedman and Briks 1946, Davison 1957, Cameron 1960, Schumacher and Maitra 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 Beherens (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 vapor, 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. Neugebauer (1964) used a simple torsion pendulum 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 1996).

(B) Quartz Crystal Monitor

In this method for the measurement of thickness of the film a sensitive
and rugged microbalance is used based 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 1996).

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
behavior of the film-substrate combination shows an oscillatory behavior 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 $n$, onto a film of index $n_1$ and thickness $t$, deposited onto a substrate of index $n_2$ with $n_1$ lying between $n_1$ 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 result) 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. Weiner (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 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 \( \upsilon/\lambda \) 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

\[ t = \left( \frac{m}{2} \right) \Delta \lambda \]

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 \( \text{Å} \) can be measured by this method (Goswami 1996).

3.2.6 Present Method of Thickness Measurement

In the present study gravimetric method was used for the measurement of thickness of the film. A single pan balance (K. Roy, Varanasi) having least count of 0.0001 gm was used. It has been observed that the film thickness increases with the increasing dipping time. The behavior of total thickness is shown in fig.-3.3. The thickness varied from .2 \( \mu \text{m} \) to .4 \( \mu \text{m} \) for dipping times between \( \frac{1}{2} \) hr. to 2 hrs. The highest photoresponse was found for a dipping time of 60 minutes and thus in most of the studies the films were prepared at this time.

3.3 Measuring Arrangements

To describe the photoconducting properties of the thin films coplanar electrodes of 2mm width and 24 mm length using colloidal silver paint were applied on the surface of the film at a separation of 2mm. The details of experimental arrangements for the various studies included in this thesis are described below:

3.3.1 Rise and Decay Studies:

A set up described in fig. 3.4 was used for these studies. A 100 W commercial bulb was used as an excitation source and regulated power supply (Unitec, Scientifec Equipments, Roorkee) for biasing purposes was used. The corresponding
FIG. 3.3 VARIATION OF THICKNESS WITH DIFFERENT DIPPING TIMES FOR THE FILM - (Cd$_{0.35}$-Pb$_{0.05}$)$_{S}$
FIGURE-3.4 BLOCK DIAGRAM FOR PHOTOCONDUCTIVITY RISE AND DECAY STUDIES
current was recorded by a nanoammeter (NM 122 from M/S Scientific Equipments, Roorkee). The strip chart recorder used for recording rise and decay studies is made by Systronics (Model No.1501), Ahmedabad.

3.3.2 Intensity Variations

For intensity variation calibrated neutral density filters were used. A Philips Infraphil (HL 4307) source was used as an infrared source. For the supply of UV light, a Philips 80W mercury bulb was used.

3.3.3 Spectral Studies

(i) Photoconductivity Excitation Spectra

For the study of photoconductivity excitation spectra light, from a commercial 1KW bulb was used as an excitation source. The light was focused on a prism monochromator and then finally the dispersed light was allowed to fall on the photoconducting cell. The thus produced photocurrent was recorded by a digital nanoammeter (DSN-121, Scientific Equipment, Roorkee). In this study photocurrent as a function of wavelength of light was recorded. The wavelength was changed by rotating the drum of the prism monochromator. The monochromator used was a constant deviation spectroscope (AS 17950 from MJS Andhra Scientific Co., Machlipatnam), which uses a glass prism as the dispersing medium and can be used in the spectral range of 400nm to 700nm. The monochromator was standardized with the help of prominent spectral lines of mercury discharge tube. It was finally adjusted for optimum performance by keeping the width of the entrance and exit slits equal (Parker 1968). Proper corrections of the spectra were incorporated by a method suggested by Bhushan and Sharma (1988). The experimental set up for spectral studies are described in fig.-3.5.

(ii) Optical Absorption Spectra

For recording optical absorption spectra a Varian (UV -VIS) DMS -100 spectrophotometer was used in the 400 nm- 700nm range. For the absorption measurement, the beam was allowed to enter the film through the glass substrate. These studies were made in the School of Studies in Geology of this University (Pt. R.S.S. University, Raipur).
FIGURE 3.5 BLOCK DIAGRAM FOR PHOTOCONDUCTIVITY (EXCITATION) SPECTRAL STUDIES
(iii) **Photoluminescence Studies**

For photoluminescence studies, excitation source used was 365nm line of high-pressure mercury vapor lamp filtered by Carl Zeiss interference filter. Light output was detected by an RCA 6217 photomultiplier tube. A regulated power supply (EHT 11, Scientific Equipment, Roorkee) at 1000 volts was used for supplying voltage to the photomultiplier tube and the integrated current output was recorded by a polyflex galvanometer ($10^{-9}$ A/mm). Schematic diagram for photoluminescence brightness studies is shown in fig.-3.6. For spectral studies, a prism monochromator (AS 17950 from M/S Andhra Scientific Co., Machlipatnam, range 400-700nm) was used. Figure-3.7 shows the schematic diagram for photoluminescence spectral studies. For the photoluminescence decay studies the signals from photo-multiplier tube were fed to a storage CRO (HM 205-2, Scientific MES-TECHNIK Pvt. Ltd., Indore) through a resistor of 1MΩ.

**3.3.4 Characterization Studies**

In order to understand fully the behavior of the films, it is essential to characterize them physically, chemically and structurally. Some important and commonly used methods for characterization of the thin films are as follows:

(i) **Topography**

The different methods/ instruments used for viewing the surface of the thin films are:

(a) The Stylus Technique

(b) Optical Microscope

(c) Scanning Electron Microscope (SEM)

(d) Transmission Electron Microscope (TEM)

In Stylus Technique, 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.
FIGURE 3.6 SCHEMATIC DIAGRAM FOR PHOTOLUMINESCENT BRIGHTNESS STUDIES
FIGURE-3.7 SCHEMATIC DIAGRAM FOR PHOTOLUMINESCENT SPECTRAL STUDIES
Scanning Electron Microscope (SEM) is the most widely used instrument for obtaining topographical features of a thin film. In this study, high magnification of the order of $10^5$ can be obtained with a resolution of 30Å.

Transmission Electron Microscope (TEM) is another method which in replica mode provides the best topographical resolution ~ 20Å.

(ii) Volume Structure

The X-ray diffraction (XRD) and TEM is the most widely used techniques for the determination of crystallographic structure of the bulk of thin films. The XRD technique used for the determination of the thickness of the film 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 diffraction 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 constant, orientations and other crystallographic information.

(iii) Surface Structures

For many applications like catalysis, corrosion and work function determination, the structure of the first few monolayers of specimen is important criterion. Such surface sensitive structure analysis can be done by techniques like -

1. Optical interference, light figure reflectograms, low energy electron diffraction (LEED), field-emission and field-ion microscopy, electron reflection diffraction and electron microscopy.
2. X-ray microscopy, x-ray and transmission electron diffraction and transmission electron microscopy.

(iv) Chemical Analysis

Chemical analysis describes 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 used for chemical analysis are listed below:
1. Conventional analytical techniques such as gravimetric, volumetric, polarography, radioactivation and chromatography.
2. Optical spectrography.
3. Calorimetry, absorption and emission spectrophotometry.
4. X-ray fluorescence and electron-probe X-ray microanalyzer.
5. X-ray and electron diffraction.

Some of the instruments used are as follows:

3.3.5 Present Methods

In the present work XRD and SEM studies were undertaken as follows:-
XRD studies were made at RSIC, Nagpur by using a computerized Philips diffractometer with CuKα radiation. Further SEM studies were performed at BSIP, Lucknow using LEO (430) Scanning Electron Microscope.