CHAPTER II

Equipments used and Details of the Experimentals

Chapter II

Equipments used and Details of the Experimentals

2.1 Introduction

Various ambient and growth conditions need to be appropriately balanced for preparation of thin films of some desired quantity. Taking into consideration of the growth conditions a thin film is characterized for its various physical attributes. The quality of a thin film prepared for any desired application purpose depends on the reproducibility and consistency of its physical characteristics. Owing to its thickness a thin film does not possess sufficient mechanical strength to support itself. Hence a supporting material known as substrate is needed for deposition of thin films. It is essential that surface of the substrate in which a thin film is to be deposited be suitably cleaned so that no intervening material medium of dirt, water vapour layer etc remain in between the substrate surface of the thin film grown on it. Apart from this, the crystallinity or amorphous nature of the substrate material also plays significant roles on the structural properties of the grown thin film. In the design of the experimental procedures, all these important points have properly been taken into consideration.

X-ray diffraction method was used to identify the growth orientations and the crystal structure of the films. The surface morphology of the films was studied by using a scanning electron microscope attached with an EDAX analyzer to measure quantitatively the stochiometry of the deposited films.

A suitably designed and assembled multiple beam interferometer (Tolansky) was used for thickness measurement, with an accuracy of ±15Å where photograde silver was used for step formation. For all types of electrical and optical measurements the films were kept suspended freely in a well shielded and continuously evacuated glass tube. A series of highly stable dry cells, each of emf 9V was used to apply the bias voltages across the films. A 250watt tungsten halogen bulb having a focusing reflector was used for white light illuminations and by using a series of (51 numbers) C-Z metal interference filters, monochromatic radiations were obtained from the same white light source. With the help of sensitive Aplab luxmeter (5011S) intensities of these radiations were measured. The dark and photocurrents through the CdSe thin films were measured by an

ECIL electrometer amplifier having high ($10^{14}\Omega$ and higher) input impedance. Higher ambient temperatures were obtained by a properly designed heater powered by a variable stabilized a.c. source. The temperatures were measured with the help of a copper-constantan thermocouple sensor in conjunction with a digital microvoltmeter assembly. All these experimental arrangements along with the experimental measurement techniques are described in details in this chapter.

2.2 Film fabrication

2.2.1 Sample material used for film deposition

Highly pure bulk samples (99.999%) of CdSe obtained from M/S Koch light Co. U.K., in bulk form were used as the source materials to prepare thin films. The samples were kept inside well cleaned dry desiccators. Before every deposition the samples were crashed into very fine powder. For electrodes highly pure aluminum procured from the same laboratory of U.K. was used, while for deposition of over layer coating on the films required for the thickness measurement, photo grade purity silver (99.999%) obtained from M/S Johnson and Matthew Co. London, was used. Tantalum sheet of best quality procured form the M/S Hind High Vacuum Co (Pvt.) Ltd. Bangalore, of thickness 0.1mm, after cutting in appropriate size was used as the heater boats for evaporation of both CdSe and silver. For deposition of the aluminum electrodes good quality tungsten spiral coils designed according to the need was used (wire diameter 0.5 mm).

2.2.2 Substrate material

Basically a substrate is a perfect insulator material used only to provide some kind of mechanical support to the films with sufficient adhesion but without any chemical interaction with the film material. The surface of the substrate itself plays a major role in the nucleation and the growth process of the films and thereby influences the film properties considerably /1/. An ideal substrate is expected to posses the following properties /2/,

(i) the surface should be flat and smooth.

(ii) neutral to different chemicals used in processing.

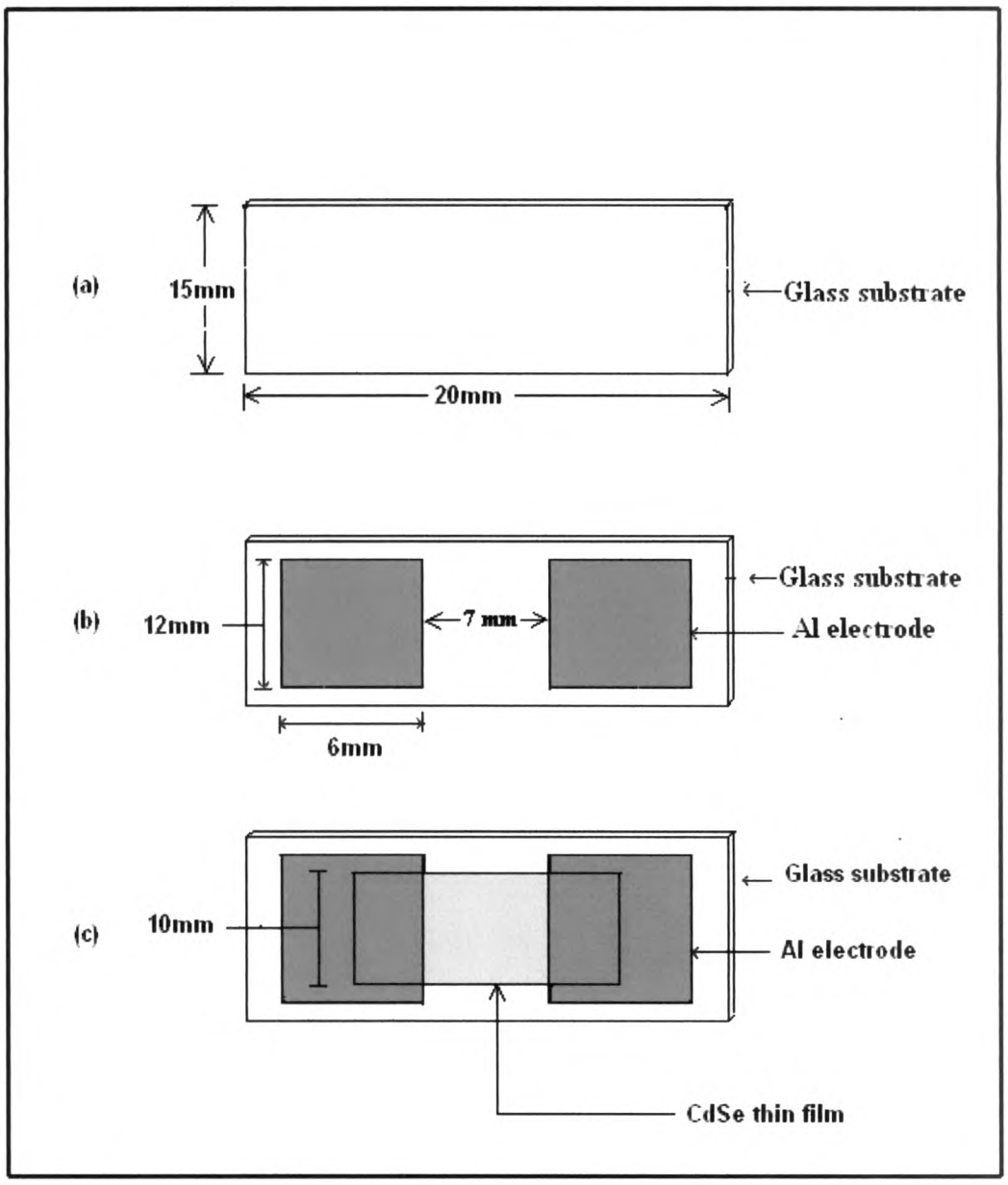

Figure 2.1 Construction of gap type cell configuration (Al/CdSe/Al structure).

(a) Empty glass substrate.

(b) Glass substrate with aluminium electrodes.

(c) Glass substrate with aluminium electrodes and CdSe thin film for gap type cell configuration.

(iii) high thermal conductivity.

(iv) high electrical resistivity in order to prevent current leakage between different circuit elements.

(v) high mechanical strength to withstand strain in processing and mounting.

(vi) nearly same coefficient of thermal expansion with that of the film material to minimize the thermal stress.

(vii) zero porosity to minimize outgassing and to ensure film uniformity.

Polished micro-glass slides, ceramic plates, mica plates, any cleaved crystal face etc are generally used as substrate for growing films. Although no substrate possesses all these properties together, depending on the purpose, any substrate material satisfying some important requirements may be used after proper treatment. Glass is widely used as substrate material for the deposition of polycrystalline films. In the present case to deposit CdSe films microscopic glass slides, (Blue Star) manufactured by the Polar Industrial Corporation; Mumbai were used because these fulfill most of the requirements of a good substrate like smooth surface, good adhesion, better thermal stability over wide range of temperature (77 to 500K), high electrical resistivity /3/ ($\sim 10^{15}$ ohmmeter) compared to sample materials, chemical inactivity and so can be cleaned by chemical method, etc.

The glass slides used in this work, which were cut out with the help of a diamond head glass cutter from micro glass slides of size (75 x 25 x 1.4) mm^3 for different types of measurements are of following dimensions,

(i) thickness measurements : (7 x 6 x 1.4)mm^3

(ii) electrical measurements : (20 x 15 x 1.4)mm^3

(iii) optical measurements : (20 x 15 x 1.4) mm^3

(iv) XRD analysis : (20 x 15 x 1.4) mm^3

(v) SEM studies : (7 x 7 x 1.4) mm^3

In Fig 2.1 and Fig 2.2, these different types of glass substrates are shown schematically.

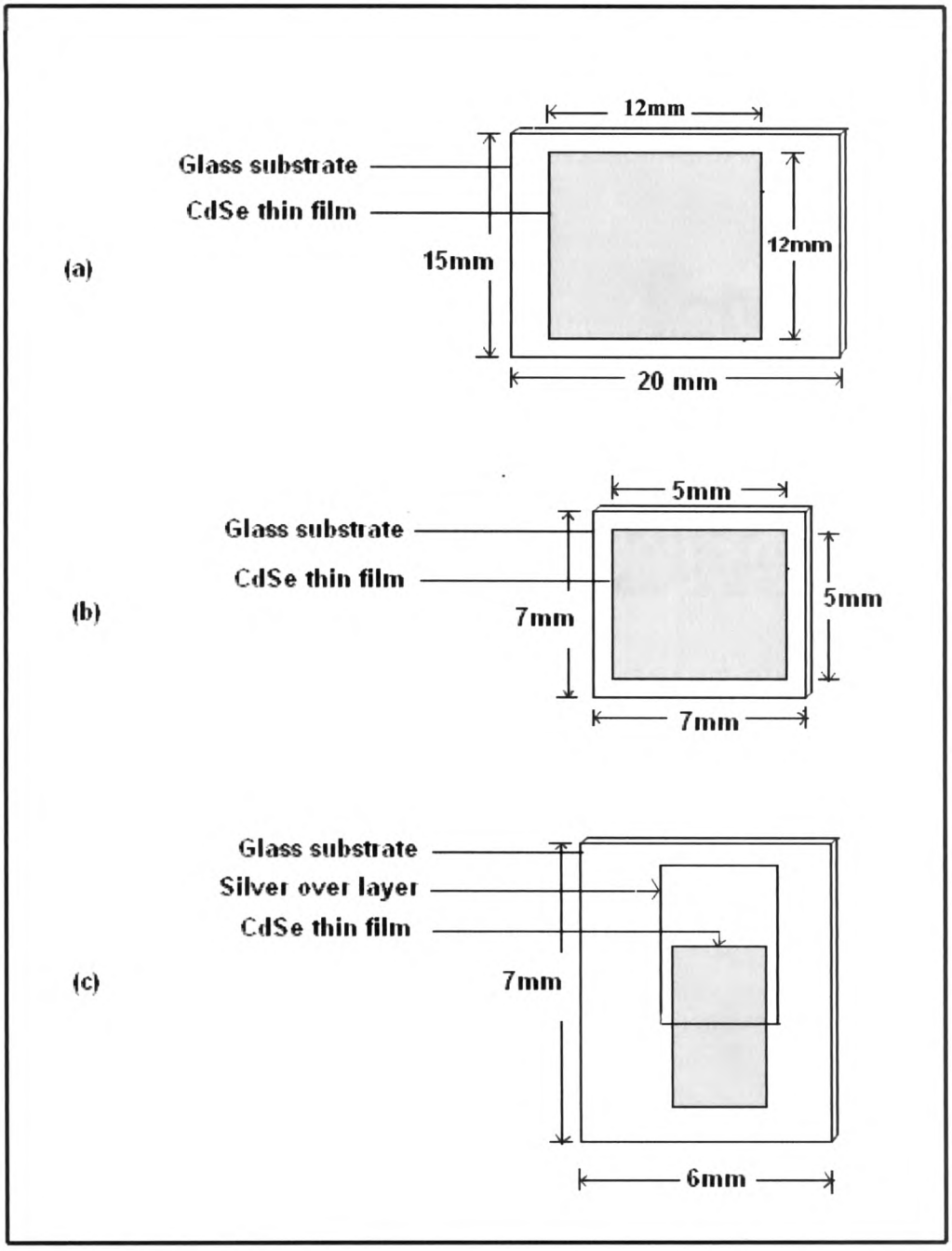

Figure 2.2 CdSe thin film on glass substrate used for

(a) XRD analysis

(b) SEM analysis

(c) thickness measurement.

2.2.3 Substrate cleaning

As has already been mentioned a properly cleaned substrate is a essential to grow good quality thin films. Usually dust particles, fingerprints and sticking of different impurities and oily layers are the main contaminants on the glass to be used as substrates. Different effective methods of cleaning are used for substrates of different nature /4,5/. The use of chemical reagents either acids or alkalis of proper concentrations are useful to remove various contaminants by breaking the bonds that might form between the contaminant molecules and the substrate surface. Since chemicals like hydrofluoric acid, caustic soda and potash readily attack glass surface, chemicals are carefully selected to clean the glass substrates. The ultrasonic cleaning is another recommended process for removing gross contaminants such as greasy particles and fingerprints. The procedure enhances the dissolution of residues strictly on the substrate by the intense local stirring action by the shock waves created in the solvent. The substrate cleaning procedure adopted in this work is elaborated as follows.

The glass substrates cut into appropriate sizes were initially washed with ordinary detergent solution to remove gross contaminants and then these were kept immersed in dilute nitric acid for about twelve hours. Taking out of dilute nitric acid, the substrates were washed properly by freshly prepared distilled water and then kept immersed in freshly prepared chromic acid for about half an hour at a temperature around 40^0–50^0C (mild heating). Taking the substrates out of the acid, these were washed thoroughly by distilled water, then gently rubbed with wet filter paper swabs and after that these were again rinsed by double distilled water. Finally the subtracts were cleaned by the ultrasonic cleaning method. The distilled water required for these purposes were prepared in the laboratory with the help of an all glass distillated water plant assembled in the laboratory depicted in Plate 1. The ultrasonic bath has been shown in Plate 2.

The drying of wet and cleaned subtracts is also critical because of probable recontamination due to absorption of gaseous particles and dust. So necessary precautions were taken in this regard. Taking out the substrate from the ultrasonic bath, these were thoroughly washed by double distilled water then they are put vertically in a clean corning glass beaker, such that surface of the substrate do not touch any where else. It might be ensured that no water strain mark on the substrate surface was left after drying.

The substrates were dried in this configuration by keeping the beaker, closing its top by a pettry dish, inside a cleaned and closed stainless steel oven, devised for this purpose.

The substrates were handled with clean grease free tweezers throughout the cleaning process. Immediately after drying, the substrates were mounted on the masks which were prepared in required size and placed inside the glass belljar of the vacuum coating unit. But before that cleanness of the glass substrates were tested by a visual examination using oblique illuminations. The loaded substrates were then heated up to 473K in a vacuum of 1.33×10^{-4} Pa for about one hour by the radiation heater of the coating unit. This was done before each batch of film deposition so as to reduce the contamination due to absorbed gas layers to a possible minimum and thus to obtain good adhesion of the films on the substrates /6/. Finally the substrates were allowed to cool down slowly in-situ to room temperature after which the depositions were carried out.

2.2.4 Masks preparation

A mask is a suitable shaped aperture to facilitate deposition of the designed film pattern. The marks were cut to required pattern from freshly cleaved good quality mica sheets with the help of 'Draffman cutter' (Allied Industries Pvt. Ltd. Bombay) and razor blades. Three types of masks were mainly used, which were for (i) film deposition (ii) electrode deposition (iii) step formation in thickness measurement. Fig. 2.3 shows a schematic arrangement of these masks.

The masks for film deposition were designed such that it can accommodate the deposition of six films at a time. Out of these six films, one was for thickness measurement, one for SEM observations, another one for XRD studies and remaining other three were for photoelectric studies. The film for XRD studies was also used for optical absorption studies. The optical absorption studies were done before doing the XRD analysis of the film. Designing and positioning of the mask might ensure that all the films were of uniform thickness. The masks were placed inside the vacuum chamber in close proximity to the substrates and with its center normally above the source heater. Earlier the masks were cleared by using acetone, and then dipped them into dilute nitric acid for 10 minutes. These were then again dipped in freshly prepared distilled water for about 30 minutes and after that washed thoroughly by distilled water. Finally these were

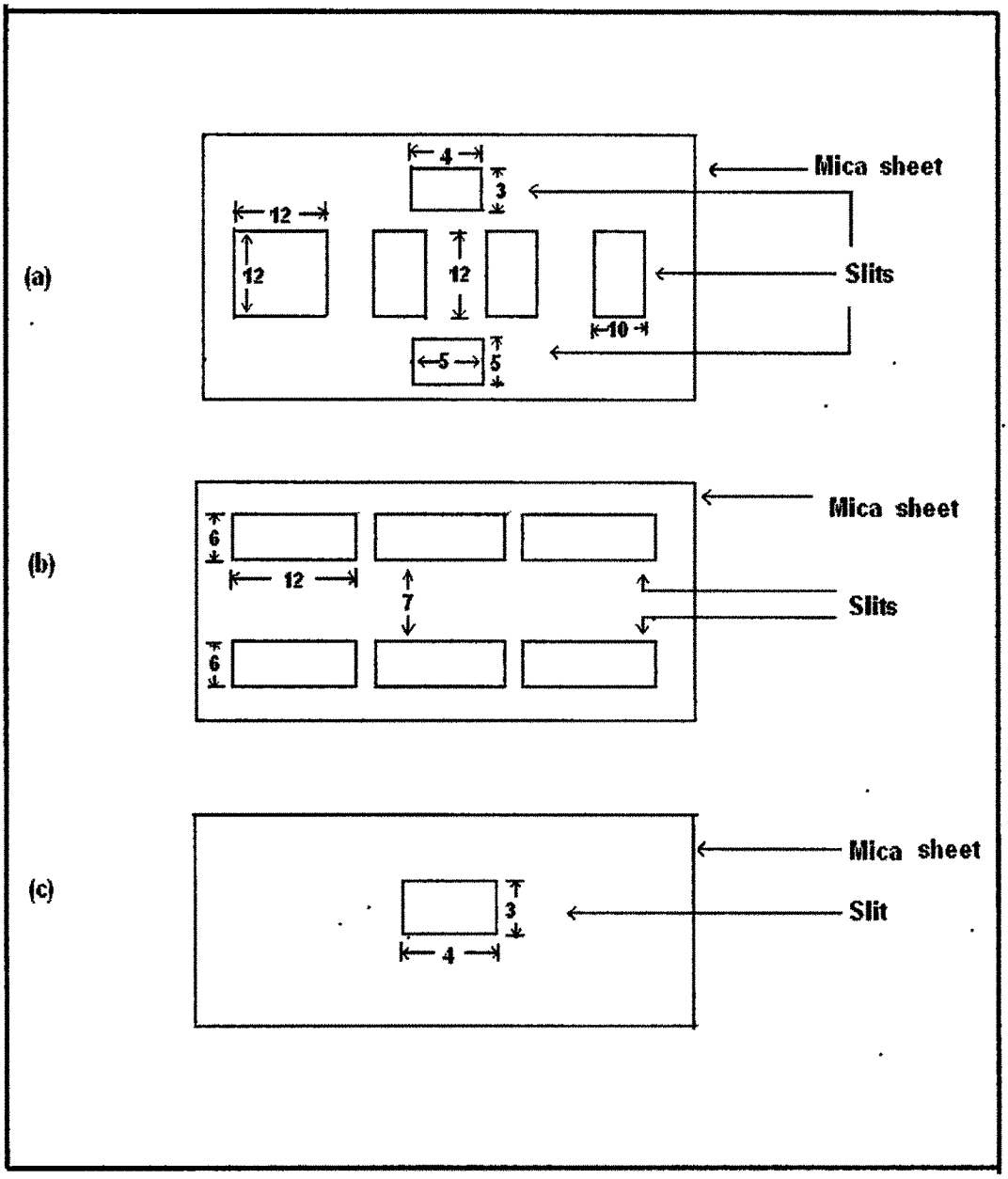

Figure 2.3 Schematic diagram of arrangement of masks (all dimensions are in mm).

(a) Film deposition

(b) Electrode deposition

(c) Step formation for thickness measurement.

dried properly in a clean dust free environment and loaded in the deposition chamber of the vacuum coating unit, in between two suitably designed aluminum mask holders which were also cleaned in a suitable manner.

2.2.5 Substrate heating

The semicircular radiation heater positioned above the substrate holder assembly in the vacuum chamber, had been used to raise the temperature of the substrate to any desired value (upto 673K). Substrates were so placed that they lies on the center plan of the semicircle. The power to the radiation heater was supplied and controlled from outside through an autotransformer. The thermo emf was measured with the help of a copper constantan thermocouple in conjunction with a digital microvoltmeter (DMA 5001) procured from M/S Scientific Equipment and Service, Roorkee. The corresponding temperature was evaluated by a calibration curve (corrected to room temperature) between temperature and thermo emf.

2.2.6 Vacuum coating unit

For physical vapour deposition - thermal evaporation high vacuum is the most essential requirement, because it can minimize the interaction between the residual gases and the sensitive surface of growing films. A few necessary factors for vacuum evaporation system are

(i) sufficiently low threshold pressure.

(ii) fast achievement of threshold pressure from atmosphere.

(iii) a working chamber free from any kind of contamination.

(iv) spacious and easily accessible working chamber.

(v) the possibility of installation of a sufficient number of electrical feed throughs into the working chamber and possibility of transmission of motion inside the chamber from outside.

For the purpose of electrodes and thin film depositions a conventional vacuum coating unit (Hindi High Vacuum; Bangalore, model 12A4 HINDHIVAC) had been used (Plate 3). The evacuation of the chamber was made by an oil diffusion pump of 10.2 cm diameter having a speed of about 50 lit /sec backed by a double stage ballast rotary pump

which had a suction capacity of 3.5 lit/sec. For the diffusion pump dow corning 704 silicon fluid was used which could produce a vacuum in the range of 10^{-5} to 10^{-7} torr. The rotary pump alone could give a rough vacuum of about $5x10^{-3}$ torr and thereafter by using the oil diffusion pump the further reduction of pressure was achieved. The rough and high vacuum was measured by a Pirani and Penning ionization gauges respectively. Since the coating unit was placed inside a well cleaned room and humidity was lowered by using two air conditioners, vacuum of in the range 10^{-5} to 10^{-6} torr could be achieved. The diffusion pump was connected to the chamber through a water cooled isolation value known as the baffle valve, which could adequately baffle the diffusion pump against the direct entry of oil vapour molecules into the chamber.

The working chamber of the vacuum coating unit consist of a 30 cm diameter belljar made of corning glass fitted with a L-shaped neoprene gasket at its base. The belljar with the gasket was mounted upon a stainless steel base plate which was firmly joined by welding to the top of the baffler valve and was provided with a few electrodes to facilitate external electrode connections for radiation heater, power supply unit, thermocouples etc. The coating unit was provided with air admittance cum isolation valve for admitting air from outside to the working chamber whenever necessary. A mechanical shutter which could run freely between the substrate and the source by means of external lever attached to a Wilson seal arrangement, was fixed to the base plate. All the leaking parts of the coating unit were tightly fitted with neoprene "O" rings. Before every run for deposition of films and the electrode material; the glass belljar, neoprene gasket, base plate and all other components inside the belljar were thoroughly cleaned and dried by blowing hot air.

For deposition purpose the source hater (tantalum boat for film deposition and helical tungsten coil for electrode deposition) was clamped at the two ends of two copper plates which in turn were fixed at the top of the lead in electrodes inside the vacuum chamber by steel screws. It was connected to a LT supply obtained from the output of a transformer attached to the vacuum coating unit itself. The mask holders, masks and the substrates inside the belljar were normally supported with the help of three uprights stainless steel pillars fitted to the base plate.

2.2.7 Film and Electrode deposition

Generally, when the temperature of a material reaches its boiling point it evaporates. However, if the material has a sufficiently high vapour pressure before occurrence of melting, it sublimates at a temperature at even lower then the melting point and the condensed vapour forms a film. The films of CdSe were deposited by this process of sublimation. Here tantalum was selected as the boat material because it has a low partial pressure upto the evaporation (sublimation) temperature of CdSe sample. For deposition of CdSe films and silver overlayers; necessary for thickness measurements, separate tantalum boats were used.

The sublimation temperature for CdSe material is nicely achieved by adjusting the heating current in the range of 40-60 ampere keeping the filament voltage in between 30-50 volt. For deposition of films, the source to substrate distance was maintained at about 6.0 cm in order to obtain uniformity in the thickness of the films. Deposition rate was nearly 8-12 Å/sec. The deposition parameters were adjusted to produce films of different requirements.

Every new empty boat was flushed out in vacuum (~10^{-6} Torr) by passing a heavy current for a short interval of time to remove probable contamination due to absorbed gas layers. After cleaning the boat it was allowed to cool down to room temperature, required amount of specimen powder was poured into the boat and spread smoothly over it, such that thin powder layer made good thermal contact with the boat. The powder was not allowed to touch the electrode junctions. Condensation of preliminary evaporating charge on the substrate was prevented by keeping the shutter closed. This also minimized the deposition of impurities that may be present on the surface of material to be evaporated. The temperature of the loaded boat was slowly increased, otherwise the sample powder might jump out of the boat and thus the specimen was backed at several steps to flush out air, moisture etc, keeping the shutter closed to avoid unwanted contaminations. Finally the temperature was slowly increased to the desired sublimation temperature of the sample. The shutter was then removed and after attaining the required thickness additional condensation was quickly stopped by closing the shutter again. Then heating current was reduced to zero, the LT power supply was cut off.

For electrical connection with thin film, two probe electrode system was used with aluminium as electrode material. Aluminium was selected as the electrode material because,

(i) it yields ohmic contact with CdSe thin films and no photo-voltage was found to develop.

(ii) it has high conductivity and did not react chemically with the respective film material.

(iii) it gives good adhesion with glass substrate and also has mechanical stability along with low stress /7/.

(iv) it is also not easily oxidized to form a nonconducting layer.

The electrode separation was maintained at 7 mm apart such that the film dimension was 10 mm x 7 mm. The electrode dimensions were 10 mm x 6 mm. The two probe electrode system along with the film structure on glass substrate is shown in Fig 2.1. After numerous experimental trials 7mm electrode separation was found to be suitable to eliminate the problem of contaminating the film specimen by diffusion of electrode material into the thin film matrix. For higher separation even for very high applied bias the effective current becomes very low which may not be very distinct from noise. This is particularly of great importance in view of the fact that the resistivity of these polycrystalline thin films are in the range of 10^{8} ohm meter. In such high resistive specimens even a very low leakage current of the order of 10^{-12} to 10^{-14} ampere can make an appreciable noise across the high impedance sample.

In this case to form thin film of aluminium electrodes, thin aluminium wires were evaporated from tungsten coil. As the surface of the tungsten wire is normally covered with oxygen and carbon, in order to prepare good quality films, it is necessary to clean the coil before use. These coils were cleaned electrochemically. The tungsten coils were electrolytically etched in a dilute solution of sodium hydroxide (NaOH) using a low tension battery (3V d.c.). The coil was made the anode and a tungsten wire mesh was used as the cathode. The electrolytically cleaned coils were then taken out from the solution and then thoroughly rinsed first in distilled water and then in absolute alcohol.

Silver layers, required for thickness measurement were deposited by thermal evaporation of high purity silver taken in the form of small pieces, from tantalum boat. In the deposition of silver and aluminum films, keeping the shutter closed the heating currents were slowly increased such that material melts and wets the tantalum boat and tungsten filament respectively. Then the films were deposited by opening the shutter and by increasing the current further. For silver deposition, the filament current through tantalum boat was adjusted within 60-65 amperes and for aluminum deposition; the current through tungsten coil was maintained within 20-25 amperes. Silver as reflecting coating of thickness about 1500 Å was deposited over one film, out of the batch of six films of the same run, which was later used to measure the thickness of the deposited films. The film structures along with the glass substrate, used for thickness measurement are shown in Fig 2.2.

2.2.8 Post deposition treatment

Freshly prepared CdSe thin films showed very unstable properties when exposed to the atmosphere. Therefore proper treatment to such deposited films became necessary. The CdSe thin films used for Optical observations, XRD analysis, SEM studies and Optoelectronic measurements were annealed in vacuum for two hours at a temperature of 373K. Hereafter before taking any measurements the films was stored in dry air for a definite period of time. Electrode deposition necessary for various optoelectronic measurements were done later on only to these treated selected films. These types of similar treatments helped in standardization of all the experimental CdSe thin films considered for different analysis.

2.3 Thin film thickness

2.3.1 Control of film thickness

Through several trial evaporation runs the factors affecting the rate of deposition on the substrates were tried to evaluate. It was observed that during deposition period, rate of deposition was effected by different amount evaporant on the boat, configuration of the boat, source to substrate distance, input power to the evaporation source etc. So keeping the rest of the deposition parameters as well as the other growing conditions

constant, the thickness of the deposited films were roughly controlled mainly by controlling the deposition time.

2.3.2 Measurement of film thickness

Among the prominent parameters affecting the various properties of thin films, thickness of a film plays the vital role. So accurate measurement of film thickness is very important in analyzing any property of thin film material. Different techniques are there for the thickness measurements of thin films, which make the use of different principles. For example variation of mass difference, absorption of light, interference effect, resistivity, capacitive effect, dielectric properties etc of the film with thickness. Bennett /8/ and Pliskin et al /9/ revealed that the interferometry method is one of the best techniques for the accurate measurement of thickness. The multiple beam interferometry method developed by Tolansky and his co-workers /10-12/ may be suitably used to measure the thin film thickness within the thickness range (0.002-2.0)μm with an accuracy of ±15Å, by using monochromatic light. In this method evaporation of a suitable material is made on a part of the surface or film whose thickness is to be measured so that a step or sharp discontinuity is formed at the film boundary.

2.3.3 Multiple beam interferometry method of thickness measurement

The method of multiple beam interferometry makes the use of Fizeau fringes of equal thickness for monochromatic light or fringes of equal chromatic order for that of while light. Although fringes with white light yields higher resolution and may be used to measure thickness of few angstroms, in the present case monochromatic light was used.

The thin film whose thickness is to be measured was deposited on an optically flat suitably cleaned glass substrate in such a way that it ended with a sharp edge at the middle of the substrate. This was done by suitably placing the substrate inside the coating unit on a specially designed mice mask with sharp edged pattern. A reflecting coating of silver was then deposited covering the film and the bare surface of the substrate so as to from a sharp step on the film edge whose thickness was equal to the material thickness of the film. Another thin and smooth glass plate whose one side was coated with partially transparent silver layer, called Fizeau plate was then placed over the step (composite

surface) in such a way that a wedge of air gap was formed at the step as shown in Fig 2.4(a).

A parallel monochromatic beam of light when allowed to fall normally upon the wedges of Fizeau plate and composite film system, interference fringes of equal thickness separated by half of the wavelength of light used, could be observed by a low power microscope.

2.3.4 Experimental assembly of thickness measurement

The arrangement of a multiple beam interferometer subjected to need, was suitability designed and assembled in the laboratory where a Phillips sodium vapour lamp (55W), used as a source of light, was placed inside a wooden box and the monochromatic light coming out through a circular aperture of the wall of the box was properly focused at a small pin hole, by a combination of lenses, which acted as point source. The beam of light diverged from this pin hole was made parallel by a system of collimating lens. All the lenses were placed coaxially inside a light tight metallic cylinder fitted with a rack and pinion arrangement. Lights rays coming out of the collimator was allowed to fall on a beam splitter glass plate at an angle 45^0. So the reflected rays then incident normally on the Fizeau plate placed at an edge over the silver coated films.

A sample holder was suitably designed and fabricated in order to accommodate the Fizeau plate and silver coated sample thin film assembly, with necessary angles between them. The holder was made of two brass plates with a hinge on one side. The upper plate was provided by a fine micrometer screw on the opposite side of the hinges, in order to facilitate the adjustment of the air gap. This system was properly illuminated by the parallel monochromatic light rays reflected by the beam splitter at normal incidence and viewed with a low power microscope placed vertically above the plates. The interference fringes so obtained were of equal thickness and displaced abruptly at the position of the step as shown in Fig 2.4(b). Height of this step may be evaluated by measuring the fringe width and fringe displacement; which is proportional to step height, with the help of traveling microscope arrangement. The experimental set up has been shown in Fig 2.5 and depicted in Plate 4.

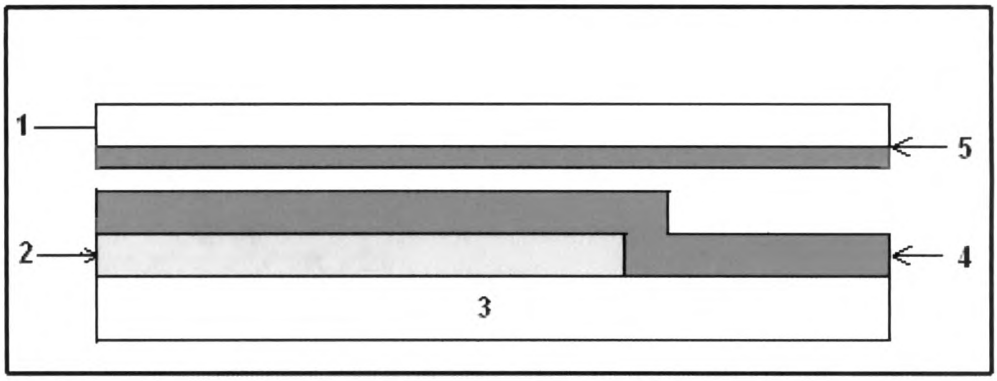

Figure 2.4(a) Arrangement for fringes of equal thickness. 1 : Fizeau plate, 2 : CdSe film, 3 : Substrate, 4 : Silver over layer, 5 : Half silvered coating.

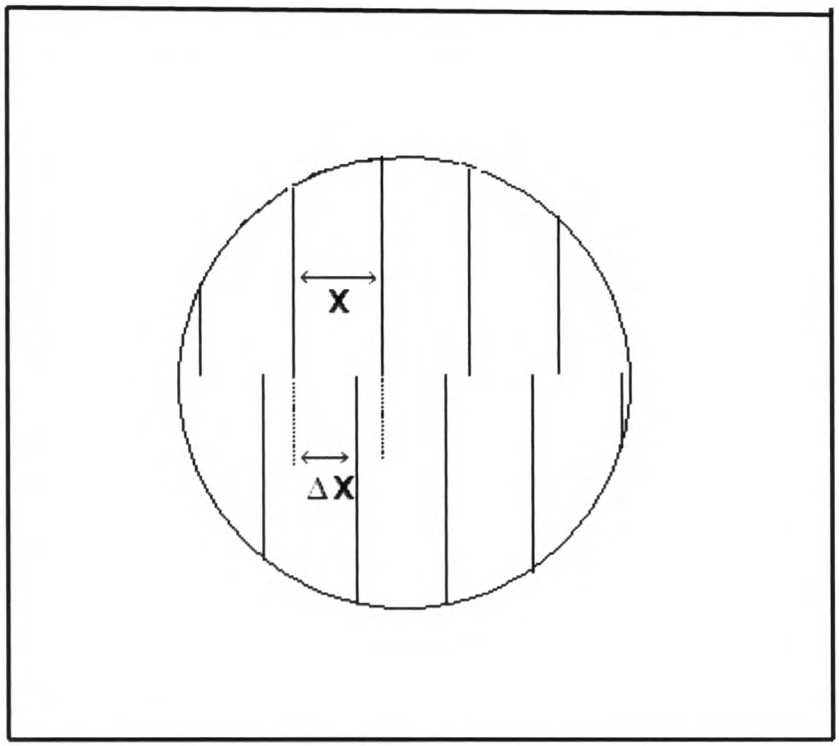

Figure 2.4(b) Interference fringes of equal thickness with fringe displacement.

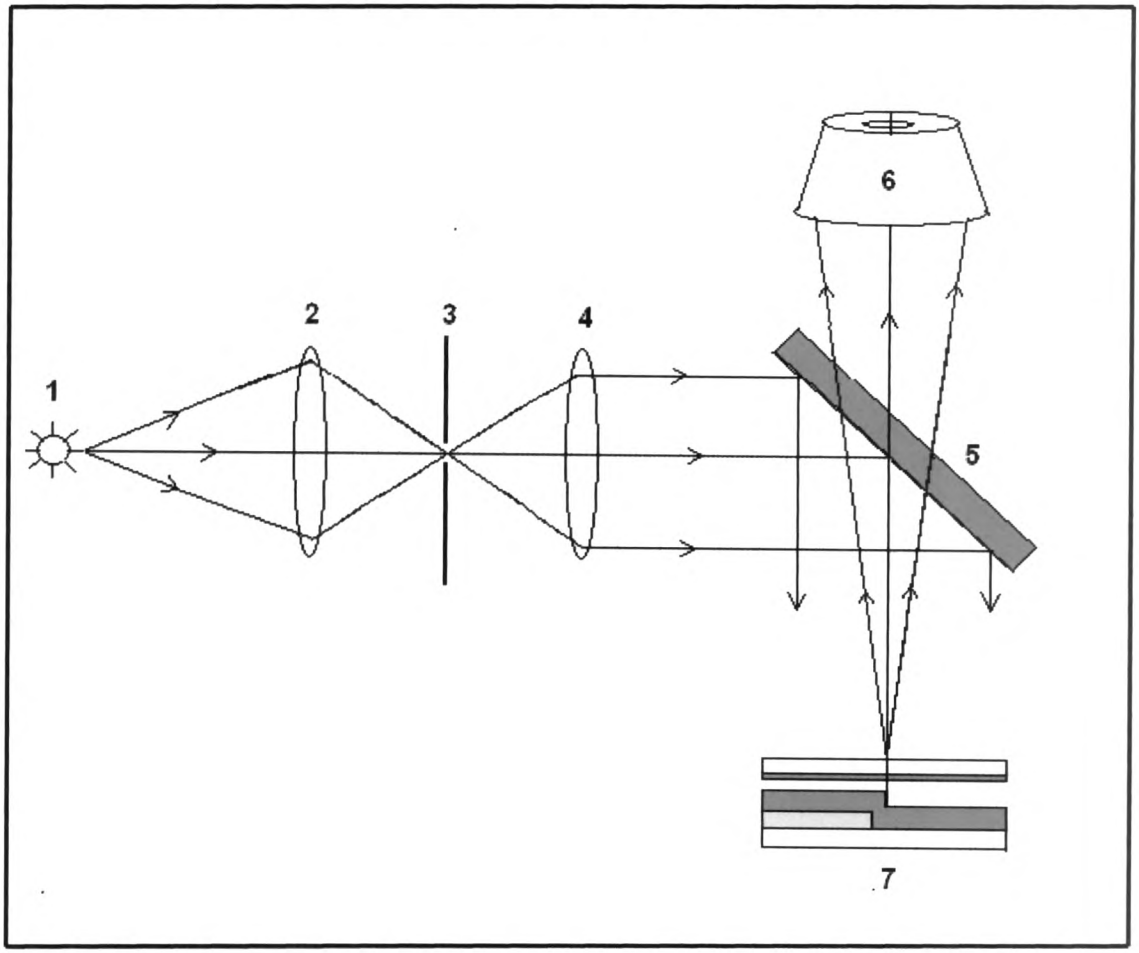

Figure 2.5 Optical arrangement of multiple beam interferometry method. 1 : Sodium light source, 2 : Focusing lens, 3 : Pointed aperture, 4 : Collimating lens, 5 : Beam splitter, 6 : Microscope, 7 : Fizeau plate arrangement.

2.3.5 Working formula

The opaque silver layer is of very low absorptivity and processes very high reflectivity (99.9%), so by making the spacing of the air gap between Fizeau plate and composite film system very small, the observed fringes can be made very sharp. In this case the phase change due to reflection is equal to π and the thickness (y) of the air-film is given by

$$y = n\,(\lambda/2) \qquad (2.1)$$

where n is an integer and λ is wavelength of monochromatic light used. When a sharp step exists, the thickness y of air gap is abruptly changed due to which additional path differences takes place between the interfacing waves and so there occurs a displacement of the entire fringe system by an amount ΔX (say). Fig 2.4(b) shows schematic drawing of a set of sharp fringes perpendicular to the step with equal displacement ΔX. This fringe displacement ΔX of the fringe system may be smaller or greater than the fringe width X, depending on the thickness, t, of the specimen film is smaller or greater then λ/2. The film thickness is given by the relation

$$t = \frac{\Delta X}{X}\frac{\lambda}{2}\text{Å} \tag{2.2}$$

Following precautionary steps are to be undertaken for accurate evaluation of film thickness.

(i) There should be a suitable thickness (approx. 1000Å) of the silver over layer used. A too thick overlayer of silver may smear out the film height; again too thin overlayer may not become fully opaque.

(ii) By suitable adjustment the air gap between the Fizeau plate and the composite film was kept as small as possible.

(iii) The beam splitter should be carefully adjusted in order to make the monochromatic parallel rays incident normally such that there was minimum divergence of the multiple beam system.

(iv) Good quality fringes manifest from smooth fair surfaces. So spectroscopic glass sides for both the Fizeau plate and the composite film were used.

(v) Sometimes, perhaps due to higher percentage of moisture particularly during rainy seasons drifting of fringes was noticed. Measurements were not taken under such conditions. Excess atmospheric moistures affect the optical thickness of the films /13/.

2.4 Design of measurement set up

The block diagram of the experimental setup to measure dark conductivity and photoconductivity at different ambient conditions is shown in Fig 2.8. The arrangement for these measurements consists of (i) Sample holder (ii) Sample heating setup (iii) Glass Jacket (iv) Current measurement setup (v) Faraday cage (vi) Optical arrangements.

2.4.1 Sample holder

A suitable sample mount system (sample holder) was constructed on a high quality mice base plate of thickness 2mm. Both top and bottom sides of the base plate was wrapped by aluminum strips which was tightened by four small screw arrangement as shown in Fig. 2.6 for better conduction of heat on both sides of the mica plate (Plate 5). On both sides of the mica plat two specially designed stainless steel strips of thickness 1mm and breath 5mm were fixed by screw arrangement and on the upper side; their free ends were made convex towards the plane surface of the mica base plate which served as the electrodes as well as pressure contacts upon the film. The film with aluminium electrodes at its ends, when placed smoothly on this sample holder below these strips in such a way that tip of the convex shaped stain less steel strips touché only the aluminum electrodes portion of the film and thus they made good electrical contacts when the respective screws were made tight.

One end of a copper-constantan thermocouple was placed on the other sides of the mica plate exactly below the sample. Before placing the film, strips were rubbed by sand paper and then cleaned chemically. On the top of steel electrodes good quality small copper strips was fixed just below the screw in order to facilitate the soldering of fine enameled copper wires, which serve the purpose of supporting as well as electrical conducting leads.

2.4.2 Sample heating

To increase the ambient temperature of the thin film sample from room temperature to any desired level (upto 523K), the sample heating was done by placing an electrical heater just below the glass jacket containing the sample holder. The input power to the heater was supplied through a variac and by changing the voltage level applied to this heater the desired temperature could be achieved. This temperature of the film was measured by a copper-constantan thermocouple whose thermo emf was recorded with the help of a sensitive digital microvoltmeter (DMA 5001) procured from M/S scientific equipments and service, Roorkee. Continuous evacuation of the glass jacket was done with the help of a rotary pump, connected to jacket, during the entire period of heating.

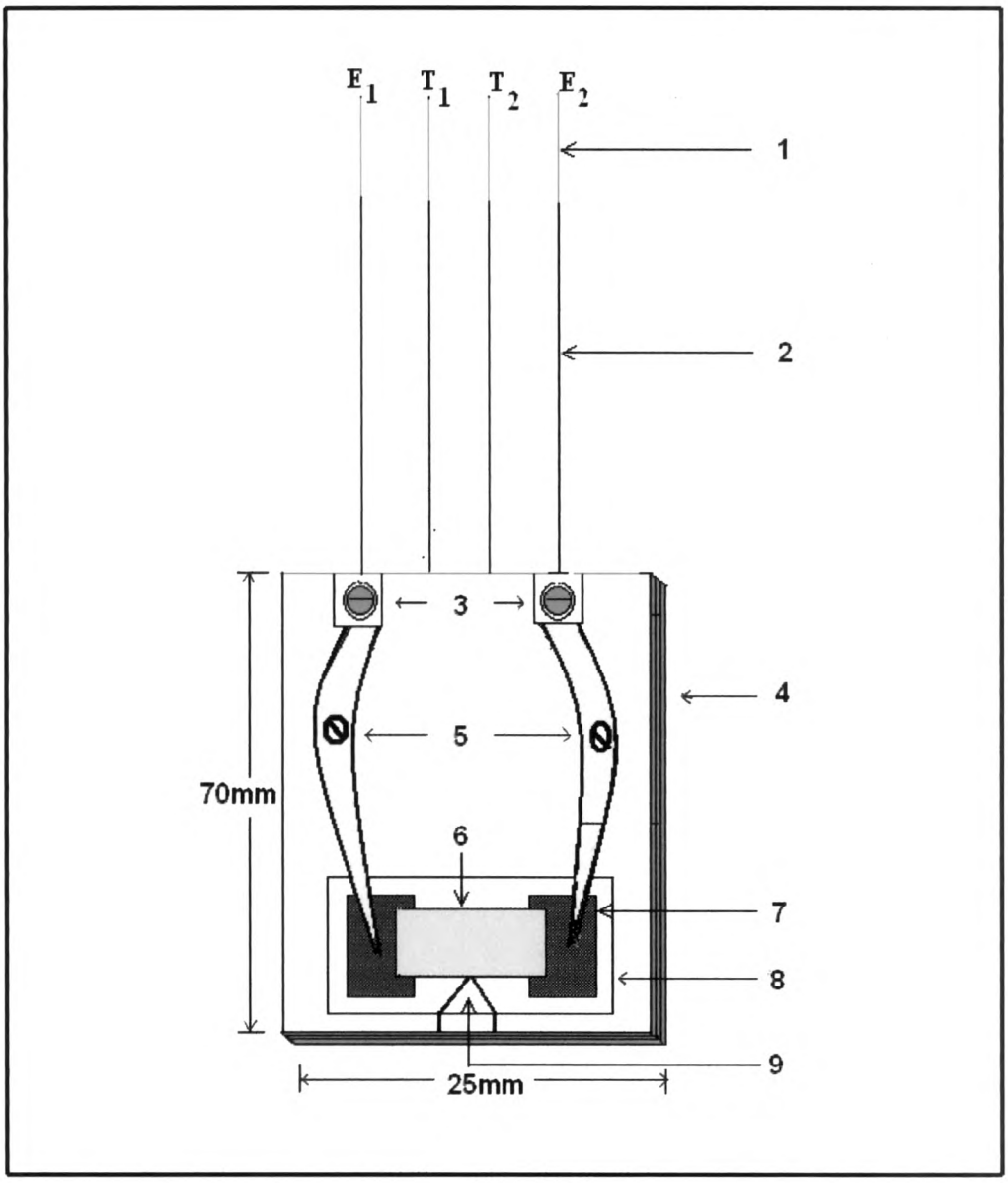

Figure 2.6 Schematic diagram of sample holder. 1 : Copper wire, 2 : Shielded copper wire, 3 : Copper strips, 4 : Mica sheet, 5 : Stainless steel strip, 6 : CdSe thin film, 7 : Aluminium electrode, 8 : Glass substrate, 9 : Copper – Constantan thermocouple

2.4.3 Glass Jacket

All the measurements related to different analysis were to be carried out in vacuum in order to minimize the effect of moisture, absorbed gas and the corrosion due to environmental impurities. For that purpose a glass jacket of total length 75 cm was constructed as shown in the Fig. 2.7 with a glass joint of size (34/35). A good quality glass stop cork with a side tube was connected to the upper side of the glass joint. During the time of measurement it was well connected to rotary pump for continuous pumping action. A perspex lid was cut out properly from a perspex sheet in a suitable pattern so that bottom face of the bid exactly fit into the glass tube and the upper face covers beyond the external surface of the glass tube. Four small holes were then hand drilled through the lid to accommodate four mutually insulated copper leads. Out of the four copper leads, two were used for electrodes connection and rest two was utilized for thermocouple connection as well as free suspension of the sample holder. Then the perspex lid with these four copper leads through it, was fitted to the top of the upper glass tube using araldite adhesive at the round glass lid interface. The holes along with the leads were also properly sealed by araldite.

The lower ends of the leads inside the glass tube were soldered to the respective wires in order to facilitate the sample holder connection. In these cases very thin wires (44 SWG) were used to reduce the heat leak through it down to the sample. The copper wire leads were mutually separated from each other by insulating hollow clips and circular mica plates. The top free ends of copper leads outside the glass jacket were well soldered by shielded copper cable for the connection of external circuitry comprising of the high impedance electrometer amplifier, digital microvoltmeter and d.c. supply unit. The glass jacket was evacuated to a pressure of $2x10^{-2}$ torr with the help of double stage rotary pump. The sample holder was made light tight by wrapping the jacket with black paper tape leaving a small window suitable for the desired illumination of the sample. It was also covered with the aluminum sheets to shield it from a.c. pick up noises. The glass jacket along with the sample holder was kept vertically at proper position with the help of suitable stand arrangement provided with clamps. The arrangement of glass jacket is depicted in Plate 6.

2.4.4 Measurement of current

For the measurement of dark current and also the photocurrent under different level of illumination of white or monochromatic light, a very high input impedance (about 10^{14} ohm and higher) electrometer amplifier (EA 815 of ECIL) was used (Plate 7). Applying d.c. bias voltage from a series connection of highly stable good quality dry cells, each of emf 9.0V, in the range (-108V) to (+108V), the potential drop across the input resistance of the electrometer in series with the film was measured.

The current passing through the specimen film is given by

Current = Measured potential drop / Input resistance

Therefore the resistance of the specimen film is obtained as

R_f = Applied bias / Measured current.

For the experimental CdSe thin films, the currents measured under different ambient conditions of the film, were of very low value (approx 10^{-8} to 10^{-10} ampere) and the measurements of such small currents encounter with large probability of error. Therefore following precautionary measurements were undertaken while measurements were done using electrometer amplifier.

(i) Coaxially shielded electrical cables were used for various connections to minimize induced currents and to provide proper electrical shielding to sample holder and other arrangements.

(ii) The electrometer and other accessories were protected from vibrations and stray field pick ups by using Faraday cage.

(iii) Two air conditioners were run in the laboratory in order to reduce the effect of moisture. Before and during the time of observation hot air was blown over the electrometer amplifier along with the input terminals. Further, the silicagel provided on the side portion of the moisture seal box was reconditioned from time to time.

(iv) To avoid malfunctioning of the amplifier due to humidity observations were taken mainly in dry days. For best results in measurements, the amplifier was switched on one hour before observations. All input power to different measuring unit was provided from a stabilized power supply.

(v) Generally zero setting for certain range of input resistance of the amplifier holds good for other ranges also. But there may be slight variation in the contact potential

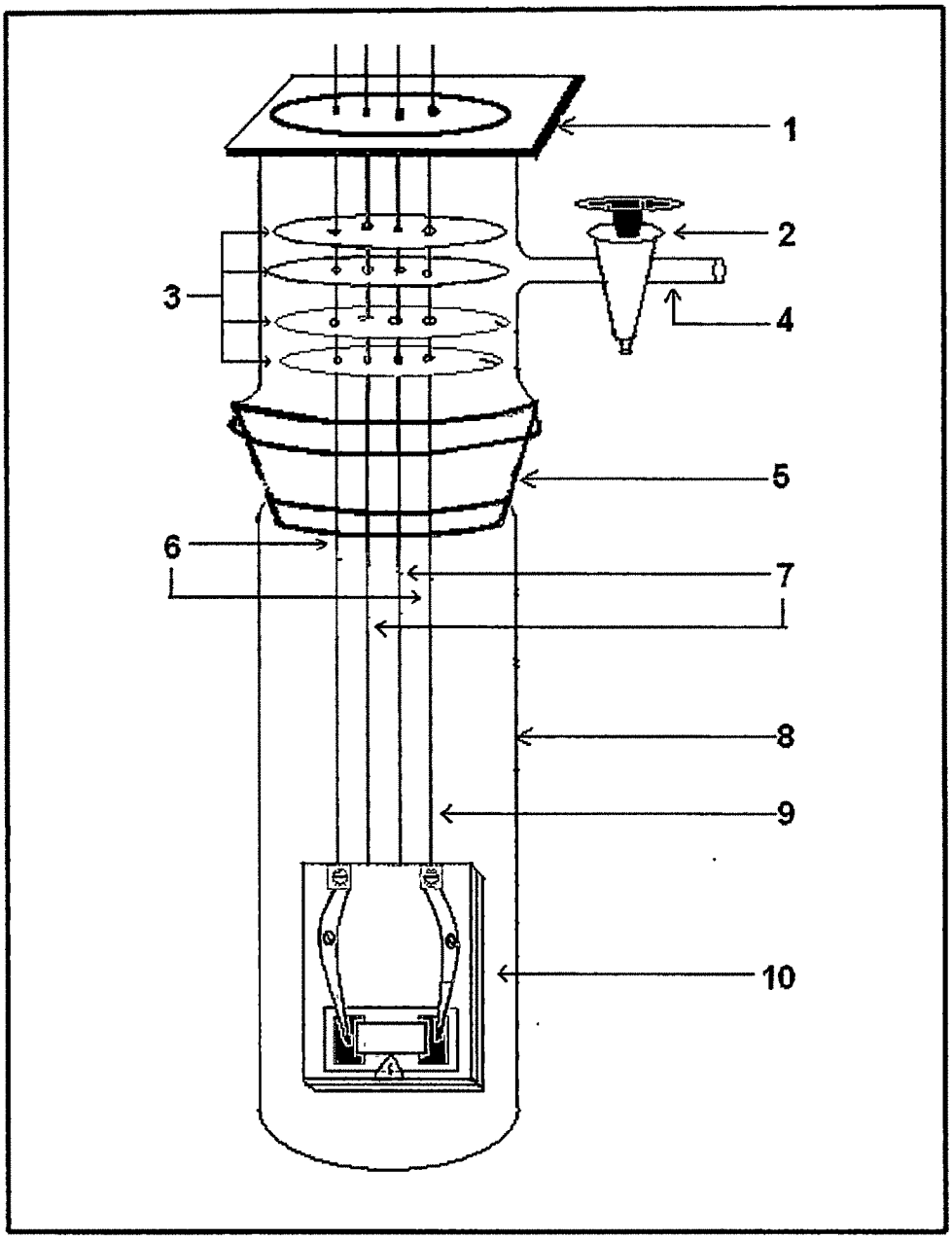

Figure 2.7 Arrangements of glass jacket, with sample holder inside, used for optoelectronic measurements. 1 : Perspex sheet, 2 : Stop cock, 3 : Mica sheets, 4 : Outlet pipe, 5 : Ground joint, 6 : Current lead, 7 : Thermocouple lead, 8 : Corning glass jacket, 9 : Shielded copper wire, 10 : Sample holder.

for different input resistance range. So a slight adjustment of zero setting sometimes became necessary, while changing the input resistance.

2.4.5 Faraday cage

The task of measuring low signal at high impedance is a tedious one and needs proper precautions. CdSe thin films prepared at different growing conditions are highly resistive and it permits only very low current to pass through it (approx 10^{-8} ampere). It was observed that when signal current was of this order pick up noise interference created a lot of problems. Therefore to avoid this type of situation a Faraday cage of proper size and shape (1.9m x 1.7m x 1.5m) was constructed using metallic nets and some triangular rods. The whole measuring unit including the observer was housed inside the cage during the period of measurements. The cage served as a massive body to shield the external noise current. All instruments and current carrying leads were properly shielded to the massive body. The entire cage was isolated from the ground by keeping it on dry non conducting wooden frame and thus it also worked as a floating ground.

2.5 Optical Arrangements

2.5.1 Optical set up

A suitable optical setup was properly designed and assembled inside the Farady cage, in order to facilitate illuminations of monochromatic as well as white light, where a tungsten halogen projector lamp of 250 watt, operating at maximum voltage 24V, procured from Sylvania Company was used as a light source. The input voltage of the source was supplied from the secondary of a step down transformer whose primary was connected to a variac. In order to have the desired glow of the lamp, the input to variac was again connected from a highly stabilized power supply. The light source was equipped with a parabolic reflecting mirror for proper focusing of light and near the source a cooling fan was placed to keep its temperature normal during the glowing stage of it. To cut off the light as desired a mechanical shutter was also used in front of the light source. The light coming out from the source was made parallel by placing in front of the source a collimating lens fixed inside an aluminum cylinder and this parallel beam was refocused sharply by an another similar lens fixed at the other end of the cylinder. The

sample was kept at focus position of this arrangement for sharp and uniform illumination while on the other side of the same arrangement there remains the source. This system is depicted in Fig 2.9. The intervening space between the focusing lens and sample film was made light tight by wrapping with black velvet cloths in order to avoid background radiations and stray light falling upon the film.

2.5.2 Filter arrangements

A series of metal interference filter obtained from C-Z instruments ltd., GDR, was used to obtain monochromatic illuminations. Out of the 64 filters (3300 – 10,012)Å only 51 were used in the experiments within the wavelength range of (4000-10,000)Å. To place the filters one at a time a filter holder, made properly using aluminum sheets was used. This holder could be well fitted with the collimating lens system to obtain monochromatic radiations. The expose time of light to the film was kept at minimum in order to avoid heating during illumination but sufficient for the photocurrents to attain its maximum value. The optical setup comprising the light source, the filter holder and the collimator was fixed firmly on a rigid iron base frame, which could move vertically upward or downward and forward or backward as desired. By this arrangement light could be suitably focused on any thin film arranged vertically inside the glass jacket on the sample holder.

2.5.3 Light intensity measurements

A sensitive luxmeter (APLAB model 5011S) was used to measure the intensity of white as well as monochromatic lights. The luxmeter could be used upto a maximum intensity of 30,000lux. Of course using two neutral density filters and some suitable arrangements the range can be increased upto 1,50,000 lux. The meter consists of a light sensing probe made of Monarica Potovoltaic Selenium Photocell covered with a thin plate of milky perspex. Its operating voltage is 9.0V d.c. The intensity of light (white as well as monochromatic) can be calibrated in terms of distance of the source and the size of the aperture corresponding to a particular applied voltage to the source through the variac. Calibration can also be done in terms of the variac voltage connected with stabilized power supply keeping source to film distance constant.

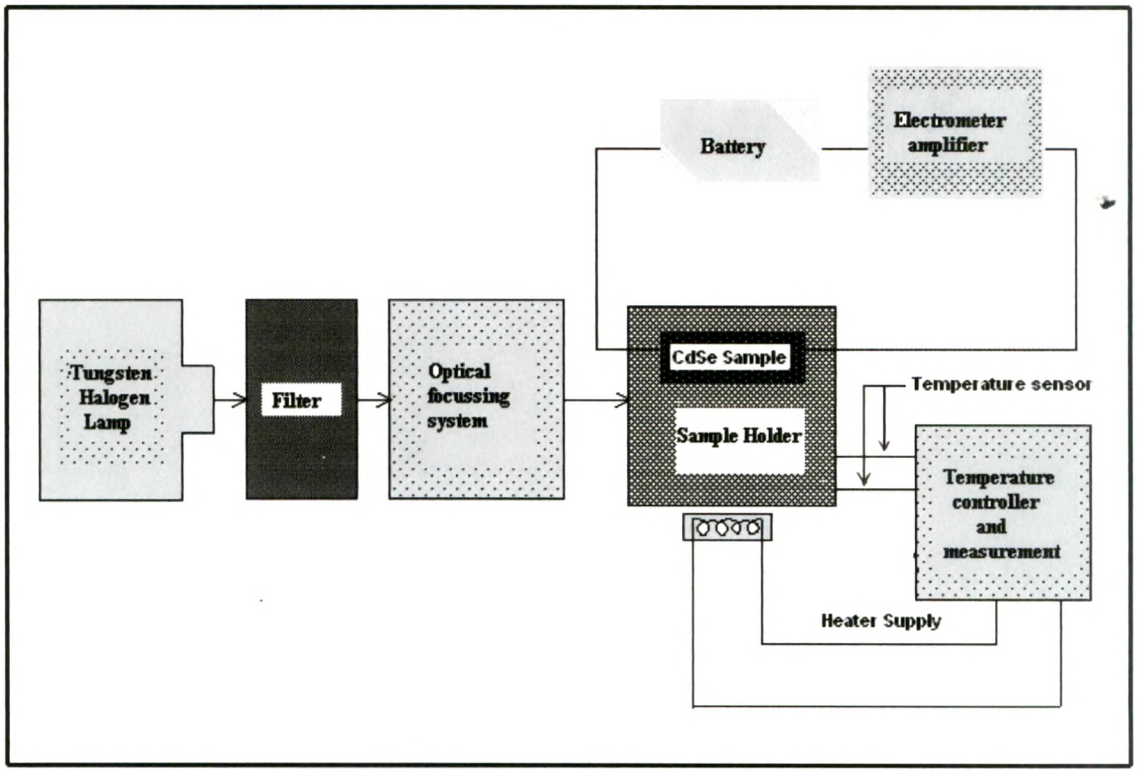

Figure 2.8 Block diagram of the experimental set up used for optoelectronic measurements.

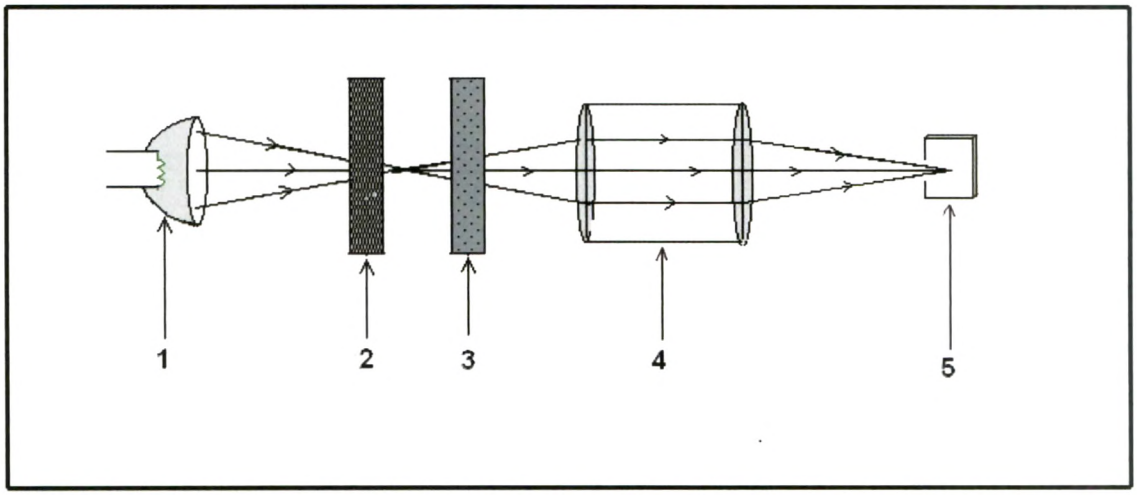

Figure 2.9 Optical focusing arrangement used for the illumination of sample. 1 : Light source (white light) 2 : Mechanical shutter, 3 ; Optical filter, 4 : Collimator setup, 5 : CdSe thin film sample.

2.6 Measurement of Transmittance and Absorbance

Transmittance and absorbance of CdSe thin films grown at different conditions were studied by using an uv visible spectrophotometer (Plate 8) in the range 300 – 900 nm (Cary 300, VARIAN, Australia). It is a double beam instrument which uses diffraction grating to separate different wavelengths of the incident light.

2.7 Structural Analysis

2.7.1 X-ray diffraction analysis

X-ray diffractogram of CdSe thin films were taken using Philips X-ray diffractometer (Philips X'Pert Pro) with CuKα radiations of wavelength 1.54056Å . The diffractometer was operated at 40 KeV and 30mA. The line profiles were chart recorded at a scanning rate of $(0.01^0–0.07^0)$ s^{-1} with a Phillips automatic recorder. X-ray diffractogram analysis including the peak search was done by computer programming using Philips X'pert software with minimum peak significance 0.65. XRD pattern of all the films as well as bulk samples were taken from 5^0 to 70^0 (2θ). For comparison, the X-ray diffractogram of bulk CdSe sample was taken which was used as the standard.

2.7.2 Scanning electron microscope analysis

Scanning Electron Microscope (SEM) is a convenient device to study the microstructure of thin films. To study the surface morphology of the thermally deposited CdSe films scanning electron micrographs of the films were taken with the help of LEO 1430VP microscope (Plate 9) with an accelerating potential 18 kV. For taking Scanning Electron Microscope micrograph, a separate film was prepared in the deposition of each batch of films. While taking the micrographs of a film different magnification levels were taken into consideration.

2.7.3 EDAX analysis

The quantitative analysis of some selected CdSe thin films deposited on a glass substrates were carried out by using EDAX (Energy Dispersive Analysis of X-ray) technique, to study the stoichiometry of the films. The elemental analysis was carried out only for Cd and Se. The EDAX analyzer is an attachment device of the aforesaid SEM.

Plate 1. Distillated water plant

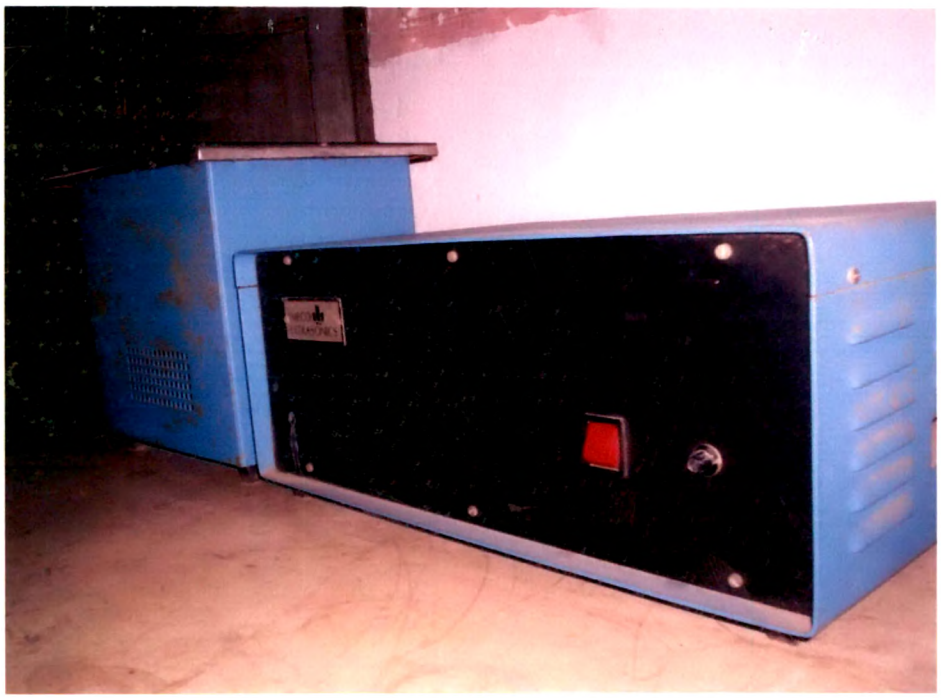

Plate 2. Ultrasonic cleaning bath

Plate 3. Vacuum coating unit (12A4)

Plate 4. Assembled multiple beam interferometer

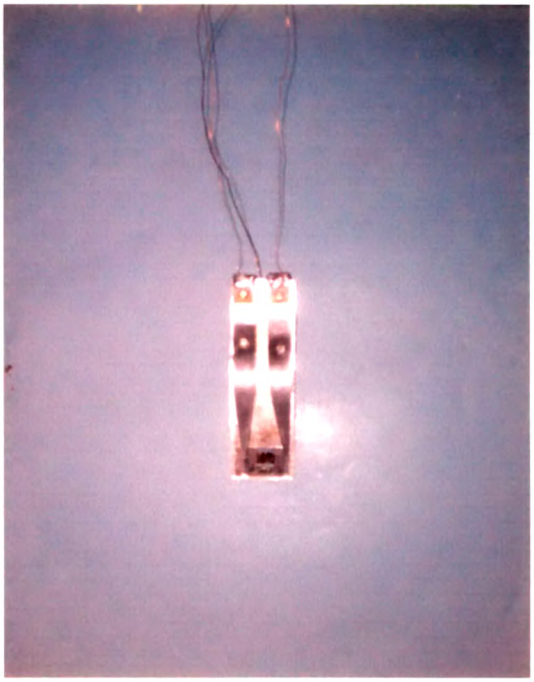

Plate 5. Sample holder

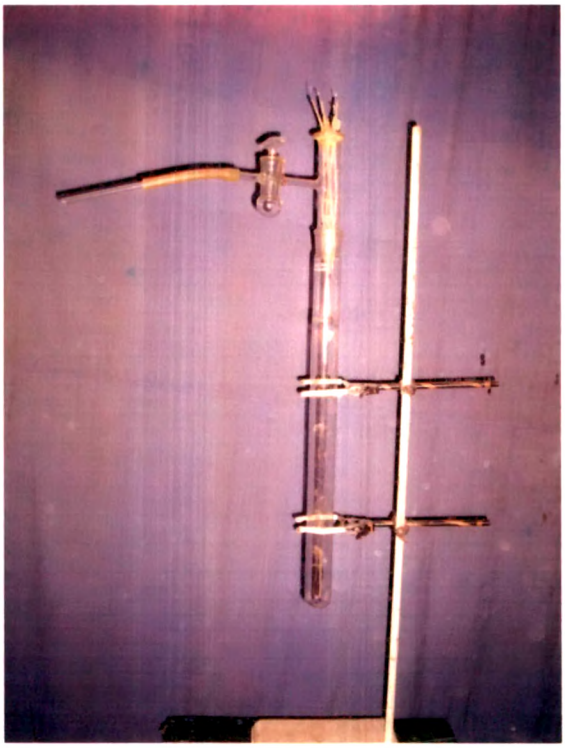

Plate 6. Glass jacket

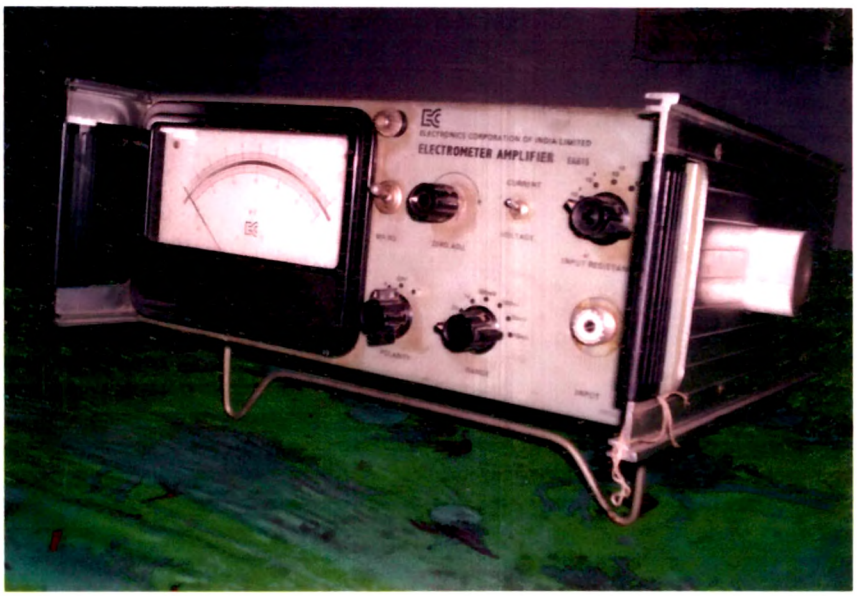

Plate 7. Electrometer amplifier (EA 815)

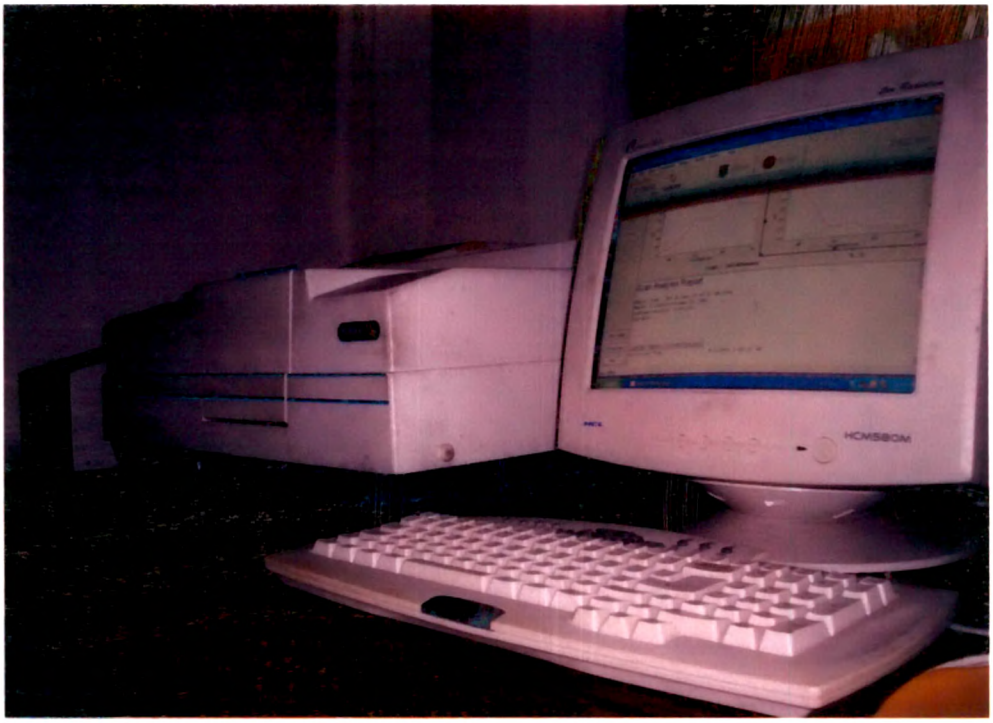

Plate 8. UV visible spectrophotometer

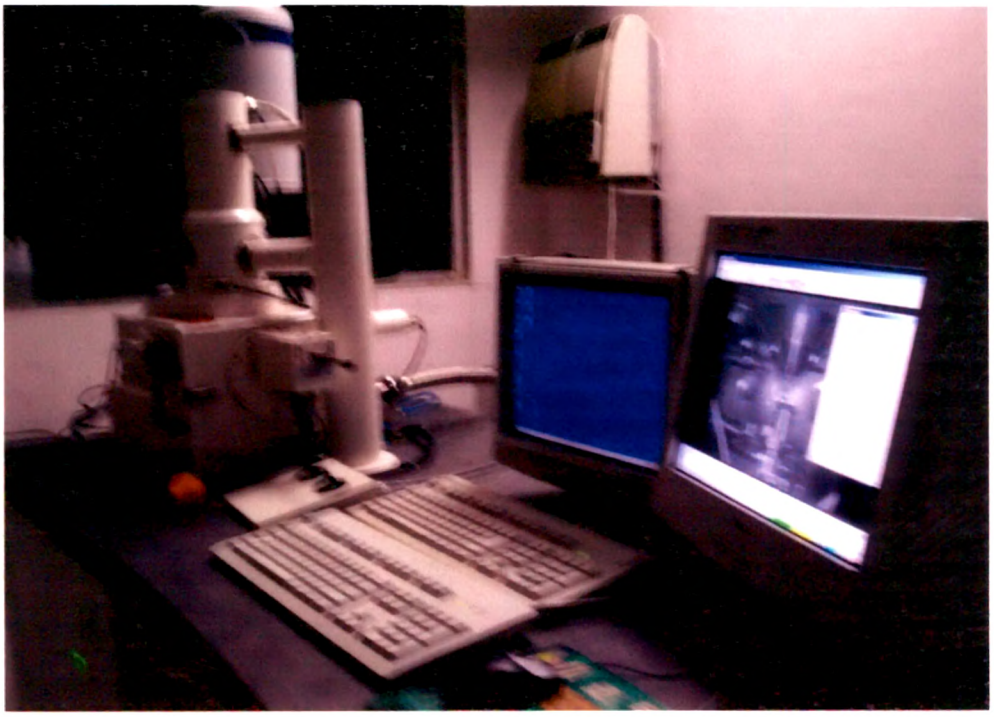

Plate 9. Scanning electron microscope

2.7.4 XRF analysis

XRF analysis was carried out with a sophisticated WDXRF (Wavelength Dispersive X-ray Fluorescence) spectrometer with atomic number 9 (Fluorine) to 92 (Uranium). In this work, a Philips Computerized Sequential XRF Spectrometer (model: AXIOS) with operated in 40kV-40mA was used for qualitative analysis of the films.

2.8 References

1. K. L. Chopra; *Thin Film Phenomena*, Mc Graw Hill Inc., New York, 1969, p 61.
2. R. Brown in L. I. Maissel and R. Glang (eds.); *Handbook of Thin Film Technology*, McGraw Hill, New York, 1970, Chap.6, p 3.
3. B. Tareev; *Physics of Dielectric Materials*, Mir publisher, Moscow, 1975, p 46.
4. R. Brown in L. I. Maissel and R. Glang (eds.); *Handbook of Thin Film Technology*, Mc Graw Hill, New York, 1970, Chap. 6, p 37-42.
5. A. Goswami, *Thin Film Fundamentals*, New Age International Publishers (P. Ltd.) New Delhi, 1996, Chap. 1, p. 45-47.
6. K. L. Chopra; *Thin Film Phenomena*, Mc Graw Hill Inc., New York, 1969, p.266-327.
7. L. Holland; *Vacuum Deposition of Thin Films*, Chapmann and Hall Ltd., London, 1963, p 100.
8. H. E. Bennet; in G. Hass and R. E. Thun (eds) *Physics of Thin Films*, Vol - 4, Academic Press, N Y, 1967, p 21.
9. W. A. Pliskin and S. J. Zanin; in L. I. Maissel and R. Glang (eds) *Hand Book of Thin Film Technology*, Mc Graw Hill, NY, 1970 chap 11-1.
10. S. Tolansky; *An Introduction to Interferometry*, Longmanns, Green and Co. Ltd., London, p 165-172.
11. S. Tolansky; *Multiple Beam Interferomerty of Surfaces and Films*, Oxford University Press, London, N Y, 1948.
12. S. Tolansky; *Surface Microtopography*, Wiley (Interscience) N Y, 1960, p 62-68.
13. H. A. Macleod and D. Richmond, *Thin Solid Films*, 37, 1976, 164.

****