CHAPTER-II

EXPERIMENTAL DETAILS AND THE MEASURING EQUIPMENTS
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2.1. INTRODUCTION

The experimental studies on the thin films require different kinds of instrumentation and measurement techniques for film deposition and characterization. To prepare a thin film of any material, one supporting material known as substrate is required. The cleanliness of the substrate surface is most important to obtain good quality thin films. In these experimental studies gap-type thin films of CdTe have been prepared onto suitably cleaned glass substrates of suitable size by vacuum evaporation method in a vacuum better than \(1.33 \times 10^{-4}\) Pa. Thickness of the film is an important parameter for the characterization and properties of a thin film. Film thickness has been measured accurately with the help of a multiple beam interferometer /1, 2/. Al-electrodes of suitable thickness were vacuum evaporated on the glass substrate prior to the deposition of the CdTe thin film to obtain a gap-type cell configuration. Both the dark and photocurrents were measured with the help of a high input impedance electrometer amplifier. Structural analysis were carried out by X-ray diffractometry (XRD) and scanning electron microscope.
(SEM). X-ray fluorescence spectrometry (XRF) studies have been used to know about the composition and impurity doping. Low temperatures were obtained by keeping the evacuated glass jacket containing the specimen inside liquid nitrogen dewar while the high temperatures were obtained with the help of an electric heater powered by variable stabilized a.c. source. Temperatures were recorded with the help of a copper-constantan thermocouple. In this chapter details of the various experimental arrangement, measurement techniques and instruments used have been described.

2.2. PREPARATION OF FILMS

2.2.1. MATERIALS FOR FILM PREPARATION

CdTe powder of purity 99.999% procured from M/S Koch-Light, England, was used as the material for the preparation of thin films. CdTe powder black in colour was observed to be in the cubic phase. The samples were preserved in a desicator. For electrodes highly pure Al was used while for overlayer coating on the film meant for the thickness measurement, photograde purity silver was used. Tantalum sheet procured from M/S Hind High Vacuum Co. (Pvt.) Ltd., Bangalore, of thickness 0.1mm was used as heater boats both for CdTe and silver evaporation. For deposition of Al electrodes tungsten spiral designed according to the need was used.
2.2.2. SUBSTRATE CLEANING

In the present investigation glass has been selected as substrate for deposition of CdTe thin films. The glass slides, used as substrates, were of dimensions $(15 \times 7 \times 1.7)$ mm$^3$ for the photoelectric measurement, $(16 \times 14 \times 1.7)$ mm$^3$ for XRD and XRF studies and $(6 \times 6 \times 0.9)$ mm$^3$ for the SEM studies.

Prior to deposition of the film the substrate must be properly cleaned. A suitable cleaning procedure was developed for obtaining the desired cleanliness of the substrates. The required number of substrates were cut into required size and then washed with detergent in tap water. The substrates were then kept immersed in dilute nitric acid for several hours. After this treatment these glass pieces were washed with freshly prepared distilled water very carefully without touching by finger. Thereafter the substrates were kept immersed for about one hour in freshly prepared hot chromic acid which was heated mildly to about $40^\circ$C or so for a few seconds. Removing these substrates from chromic acid these were again washed with distilled water. Hereafter these substrates were subjected to ultrasonic cleaning. After ultrasonic cleaning the substrates were again washed with distilled water for a long time. Finally all the glass substrates were kept vertically in a properly cleaned corning glass beaker such that the substrate surfaces do not touch anywhere else except at the two ends.
Then these substrates were dried placing the beaker inside a cleaned and closed stainless steel oven. 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. The loaded substrates were then heated upto 200°C in a vacuum of $1.33 \times 10^{-4}$Pa for about one hour with the help of the radiation heater of the coating unit. This was done always before the deposition of each batch of film so as to reduce contamination due to absorbed gas layers to a possible minimum. Thus good adhesion /3, 4/ of the sample with the glass substrate was obtained. Finally the substrates were allowed to cool down slowly to room temperature after which deposition was carried out.

2.2.3. MASKS PREPARATION

Good quality mica sheets were used as masks for the preparation of thin films. The masks were cut with the help of a sharp point knife in required sizes. Separate masks were made for the deposition of electrodes and thin films. The mask which was used for the deposition of thin film material was prepared in such a way that five films can be deposited in one batch. Out of these five films, two films were used for the photoelectronic studies, one for the XRD and XRF studies, another for SEM studies and the rest one for the measurement of thickness. The masks were freshly cleaved mica and before
their use, these were also cleaned by nitric acid and then washed with distilled water and then dried. Thereafter these were placed on the aluminium mask holder which was also cleaned in a suitable manner.

2.2.4. EVAPORATION TECHNIQUE AND INSTRUMENTATION

For deposition of CdTe thin films tantalum (Ta) boat was used as the source heater. Before each evaporation the new boat used was cleaned by acetone and then washed by distilled water and finally dried. Thereafter the boat was again heated inside the coating unit in a vacuum of \(~1.33 \times 10^{-4}\) Pa by passing a heavy electric current within a small interval of time. After the above cleaning procedure of the boat, very small amount of pure CdTe powder was spread uniformly keeping in view that the layer of CdTe powder makes good thermal contact with the bottom surface of the boat. In between the boat and the substrates a Wilson seal mechanical shutter was used so as to stop the unwanted deposition. For heating the substrates to the desired substrate temperature \((T_s)\), the radiation heater positioned above the substrate holder was used. Substrate temperatures were measured with the help of a copper-constantan thermocouple sensor. After attaining the desired substrate temperature, it was kept at constant temperature by adjusting the variac voltage during the entire period of deposition. The L.T. supply of
10V-100A used for heating the boat was obtained from the output of a transformer attached to the coating unit. From the repeated experiment it was observed that when the boat was heated quickly by increasing the heating current, CdTe powder jumps out from the boat. Therefore in heating the boat much care was taken and current was increased at slow rate. In this process, it was observed that when the current through the boat reached a value of ~ 25A, the boat began to glow. Henceforth the current was increased with extreme care to the desired value. It is to be noted that in each batch of films produced, the heating current through the boat was kept between 32A to 36A. At these currents the temperature of the source was measured and was found to be between 600°C to 700°C. The deposition rate was controlled by controlling the heater current and was measured afterwards from the knowledge of deposition time and film thickness. The rate of deposition was maintained at 2.4 — 2.5 Å/s while source to substrate distance was kept fixed at 6.5 cm for the growth of the experimental films. A conventional Hind High Vacuum coating unit, model 12A4 was used where vacuum ~ 1.33 x 10^-4 Pa could be attained. Before each deposition, the glass belljar, the gasket, baseplate, substrate holder etc. were cleaned by acetone, good detergent and fine emery paper etc. Then these were dried by blowing hot air.
2.2.5. CHOICES OF ELECTRODE MATERIAL AND DEPOSITION OF ELECTRODE

For the electrical connections with the film, two probe electrode system was used with aluminum as electrode material. The choice of aluminum as electrode material was for the following reasons.

1. It produces good ohmic contacts with CdTe semiconductor film (I-V curves in chapter-IV, Section 4.3.1.).

2. It has high electrical conductivity and good adhesion with glass substrates /5/ and also has mechanical stability along with low stress.

3. Aluminum does not react chemically with cadmium telluride.

4. Aluminum is also not easily oxidised to form a nonconducting layer.

Considering aluminum as suitable electrode material in our case from the above discussions, predeposited aluminum contacts were used for electrical measurements. The contacts for the two probe measurement were located 3 mm apart so that the film had dimension of 4 mm x 3 mm. The two electrodes were of dimension 6 x 4 mm². The two probe electrode system along with the film structure on the glass substrate is as shown in Fig.2.1.

For deposition of aluminum [Al] electrode on the glass substrate a tungsten coil of pure tungsten (W) wire of diameter 0.5mm to 1.0mm with
Fig. 2-1. A schematic drawing of contact electrode and CdTe thin film on glass substrate.
4 to 6 turns was used. Prior to its use the coil was cleaned suitably by electrolysis method using NaOH solution as electrolyte. The voltage source used was two dry cells of 1.5 volts each and the tungsten coil was used as anode while a copper plate was used as cathode. A current of about 30mA was allowed to pass through the electrolyte for about 30 minutes. Finally the coil was rinsed in distilled water and then dried. A small piece of highly pure (99.99%, Koch Light) aluminum wire was turned into a thin sheet by hitting with a clean hammer. It was then cut into small pieces and three or four pieces were hanged on tungsten coil. The deposition of aluminum electrode were carried out by passing heating current of ~20A. After attaining the desired thickness the deposition was stopped by closing the shutter and then the heating current was reduced slowly to zero.

2.3. THICKNESS MEASUREMENT AND ACCURACY OF MEASUREMENT

Film thickness was measured with the help of a suitably designed and assembled multiple beam interferometer. In the present set-up, with a proper Fizeau plate, the thickness can be measured with an accuracy of ±15Å. We may justify this from the experimental observations like:

Spacing $x$ between successive fringes can be made as wide as 5mm or so by reducing the angle of the fabricated wedge to minimum limits.
Combining very good reflectivity of the Ag overlayer, very less absorption of light by the thin optical quality beam splitter glass plate and the Fizeau plate of optimum quality, $\Delta x$ could be measured up to $\frac{1}{40}$ th of fringe separation, then the thickness of the film is given by

$$t = \frac{\Delta x \cdot \lambda}{x \cdot 2}$$

i.e. thickness $= \frac{\text{fringe displacement}}{\text{fringe width}} \times \frac{\lambda}{2}$

The accuracy of measurement is $\frac{1}{40} \times \frac{1}{5} \times \frac{5893}{2} = 15\text{Å}$

2.4. PHOTOCONDUCTIVITY MEASUREMENT SET-UP

The block diagram of the experimental set up in two point probe method to measure photoconductivity at different intensity, wavelength and ambient temperatures is shown in Fig.2-2.

Various arrangement for photoconductivity measurement consists of (a) Sample holder and electrode connection (b) Sample heating and cooling arrangement and temperature measurement (c) Optical arrangement (d) Current measurement at different ambient temperatures and under illumination of different wavelength and at different intensities.

The details of various experimental arrangements are described below.
Fig. 2-2. Block diagram of the experimental set up for photoconductivity measurement.
2.4.1. SAMPLE HOLDER AND ELECTRODE CONNECTION

The sample holder is made of corning glass with proper electrical shielding and pump line connection for creating vacuum (~2.67 Pa). The sample holder was so designed as to heat it to higher temperatures and also for cooling to liquid nitrogen temperatures. Inside the sample holder the film is attached to sample mount system made of thick mica sheet of size [50 \times 20] mm\textsuperscript{2}. The two electrodes of the film for electrical measurement can be connected to current leads [44 SWG, copper] by two pressure contact strips of steel as shown in Fig.2-3. The sample mount is kept suspended vertically inside the sample holder by four leads. Out of these leads, two were of enamelled copper wire [44 SWG] which served the dual purpose of suspension and current leads. The other two leads were a pair of copper-constantan thermocouple. The thermocouple junction was kept in firm pressure contact with the thin film. The leads were taken out of the glass jacket through a vacuum sealed teflon cork as shown in Fig.2-4. Teflon was used, as the leakage current through it is appreciably low. The glass jacket containing the sample etc. was continually evacuated to a pressure ~2.67 Pa with the help of a double stage rotary pump when the experiment was in progress. The use of very thin wires [44 SWG] as leads reduced the heat leak through it down to the sample. Light tight covering as well as shielding from a.c. pick up were made by wrapping the holder with aluminum sheets.
Fig. 2-3. Sample holder with CdTe thin film
Fig. 2-4. Sample holder assembly
2.4.2. SAMPLE HEATING AND COOLING ARRANGEMENT

The photoconductivity and dark conductivity of the films were measured under different ambient temperatures i.e. starting from room temperature to a high temperature ~120°C and from room temperature to liquid nitrogen temperatures. In order to heat the sample to high temperatures, a resistive electric heater was used, the input power of which was supplied from stabilized power supply. The sample mount jacket was kept immersed inside a liquid nitrogen dewar flask having viewing windows. The length of the dewar was 600 mm with inner diameter of 55 mm. The sample was cooled very slowly by first cooling it in the liquid nitrogen vapour and slowly allowing it to cool in liquid nitrogen. A copper-constantan thermocouple was used as temperature sensor to monitor the sample temperature from low temperature (~77K) to high temperature (~400K). The thermo e.m.f. developed by the sensor was measured by using a digital microvoltmeter (DMV-010, M/S Scientific Equipment and services, Roorkee).

2.4.3. OPTICAL ARRANGEMENT

The necessary experimental arrangement for focusing the white and monochromatic light on the sample was designed and assembled as shown in Fig.2-5. A tungsten-halogen projector lamp (250W, 24V) with a parabolic
Fig. 2.5. Optical focusing system

- Light source
- Collimator
- Light filter
- Sample
- Shutter
focussing mirror was used as the source of light. A collimating lens fixed inside a light tight cylinder of aluminum sheet was placed in front of the light source on a suitably made horizontal frame. Parallel rays of light after passing through the collimator were allowed to fall on another convex lens kept at the other end of the cylinder. Thus the emergent rays are focussed sharply and at the focal position the film was kept fixed so as to get sharp and uniform illumination on it. For obtaining monochromatic light, metal interference filters obtained from C.Z. Instrument Ltd., G.D.R., were used. The filters were placed in a light tight metal holder and were placed in between the light source and collimating lens as shown in Fig.2-5. A set of 25 filters having wavelength within the range 400-1000nm was used. The light source, collimator and filter holder were fitted on horizontal frame and could be moved up and down in the vertical position also. By this arrangement light could be focussed on any film arranged vertically inside the sample holder. A mechanical shutter was used to interrupt the light before and after illumination.

The intensity of light was measured with the help of an APLAB sensitive luxmeter (model 5011S). The luxmeter can be used to measure maximum intensity up to 30,000 lux, using two neutral density filters.

2.4.4. CURRENT MEASUREMENT

The dark current \( I_D \) and the current under illumination \( I_I \) through
the sample was very low (~10^{-9}A to 10^{-12}A). For measurement of such low currents an electrometer amplifier (EA 815 of ECIL) was used as current meter in series with the sample (as shown in Fig.2-2). The constant voltage source used was a bank of dry cells connected in series. The e.m.f. of each cell was 9 volt and the voltage was varied from 0 to 144 volts. The applied D.C. voltage across the film was measured with the help of a high input impedance digital microvoltmeter (model DMV-001 Scientific Equipment and Services, Roorkee). Since the sample films were of high resistivity and the measured current was very very low (~10^{-9}A to 10^{-10}A), special care was needed to eliminate the noise generated by different sources. The following procedure was adopted for dark and photocurrent measurements with electrometer amplifier.

(i) Coaxially shielded electrical leads were used for various connections to minimize induced currents.

(ii) A Faraday cage of large size (2m × 2m × 2m) was constructed to keep inside the entire opto-electronic measurement setup along with the observer. In order to avoid ground loop current, the grounding system was kept in floating condition. For this the entire Faraday cage was isolated from the ground by keeping it on dry non-conducting wooden frame.

(iii) To avoid malfunctioning of the electrometer amplifier due to humidity observations were taken during the days of low percentages of humidity. Hot
air was blown over the electrometer amplifier and input terminal before and during the time of observation. Similar treatment was done to the moisture seal box of the electrometer after removing the top cover. Further to keep away the damaging effects of humidity content of the surroundings, silicagel provided on the side portion of the moisture seal box was reconditioned from time to time.

(iv) For getting best result in current measurement the electrometer amplifier was switched on one hour before observation for warming.

(v) Adjustment of zero on the meter in most sensitive range normally holds good for any other range for any input resistance selected. Since there may be slight variation in the contact potential for different input resistance selection switch, a slight adjustment of the zero setting may be necessary at changing of range switch. Hence to obtain accurate measurements within the capability of the instrument, it was essential to check and adjust the meter zero prior to measurement, everytime the input resistance was changed.

(vi) All the input power to the different measuring instruments was supplied from a stabilised power supply.

2.5. ANALYTICAL TECHNIQUES AND INSTRUMENTATIONS

In order to understand about the behaviour of the deposited CdTe thin
films, they were characterized physically, chemically and structurally by using various analytical instrumentation methods available to us. The various physical properties and their measurements are discussed in detail in the corresponding chapter. A brief description of the methods adopted are described here.

2.5.1. CHEMICAL ANALYSIS BY X-RAY FLUORESCENCE (XRF) METHOD

Wavelength-dispersive x-ray fluorescence (WDXRF) spectroscopy is specifically employed for elemental analysis for atomic number 9 (Flourine) to 92 (uranium), at concentration of a few parts per million (ppm). It is used as a rapid non-destructive method for both qualitative and quantitative analysis. In the present investigation a philips computerised sequential XRF spectrometer (PW 1480) available at SIF of Gauhati University was used for some qualitative analysis of the prepared CdTe films, such as any impurity doping from evaporation source (boat material) and other source. Only qualitative analysis of the films were done and quantitative analysis at this stage was not possible due to non availability of suitable standard sample.

2.5.2. X-RAY DIFFRACTION (XRD) METHOD

Depending on the growth technique, growth conditions and other parameters, a thin film may be amorphous, polycrystalline or epitaxial in nature. The knowledge on the nature of structure of the deposited films is important
for proper interpretation of the physical, electrical, optical and photoelectronic properties of the deposited films. Various methods available for structural characterization of thin films have been described in the literature. Among the various methods XRD instrumentation technique is generally employed for whole range information such as crystal structure (i.e. epitaxial, polycrystalline or amorphous), orientation, size of the crystallites, lattice constants, composition (with the help of standards), defects and stresses in thin films. In our present investigation we used a philips automatic powder diffractometer (model APD 1700) interfaced with a personal computer (Philips 80286 PCAT) for structural analysis of the deposited films. The details of such analysis have been discussed in chapter-III.

2.5.3. SCANNING ELECTRON MICROSCOPE (SEM) OBSERVATION

For studying the surface morphology of the deposited films scanning electron micrograph of the deposited films were taken with the help of Jeol JSM-35C microscope at Regional Sophisticated Instrumentation Centre (RSIC), NEHU, Shillong. The operational voltage of the SEM was 15 KV. For taking SEM micrograph, a separate film was prepared in each batch of films. For this the size of the substrates were 6mm x 6mm.
REFERENCES


