

CHAPTER II

EXPERIMENTAL TECHNIQUES

2.1 Introduction

It is well known that various thin film properties such as structural, optical, electrical, dielectric, mechanical etc., depend not only on the purity of the material but also on their preparation technique and other parameters such as rate of evaporation, substrate temperature, annealing, the film thickness, residual gas pressure and their gas adsorption and diffusion activity. Hence for an understanding of the measured results, the deposition parameters have to be maintained constant as far as possible. In order to achieve this in the present investigation, all the depositions were carried out in well controlled conditions so that a proper evaluation of the film properties along with very good reproducibility of the different parameters could be made. There are a large number of methods for preparing thin films of different types of materials but each one has got its own limitations. Since individual atomic, molecular or ionic species of matter may exist in the vapour or in the liquid phase, the techniques of thin film deposition can be broadly classified under two main categories :

- (i) Vapor-phase deposition
- (ii) liquid-phase/solution deposition.

But generally the methods of preparation of thin films are classified as chemical and physical methods. The techniques employed

for the preparation of thin films, the substrates and masks used for film deposition, size of the thin film samples used for various studies, thickness measurement, etc., are dealt with in detail in this chapter. The experimental techniques and the methods of measurements employed in various studies have been given in the relevant chapters.

2.2 Methods of preparation of thin films

The two major categories of chemical methods of deposition are electroplating and chemical vapour deposition [1]. Electrolytic deposition, electroless plating and anodization come under the former, while pyrolysis, hydrogen reduction and polymerisation fall under the later. There are several advantages in chemical methods of deposition techniques, notable among them being the deposition rate which can be made high, and hence the film can be grown quite thick. But the main disadvantage is the difficulty of process control.

Physical method of thin film preparation is the most widely used one for various industrial applications. The most important features of PVD technique is that the transport of vapour from the source to the substrate takes place by physical means. It is also possible to achieve high deposition rates. In electronic and optoelectronic applications, this method is preferred. Fabrication of multilayer structures like interference filter and antireflection coatings will be easier by physical methods. Also

in physical methods since all the coatings are carried out in high vacuum, very clean production environment, which is very essential in the fabrication of electronic devices can be maintained. Ultimately physical deposition is a clean method of film preparation in the sense that no chemical solution is used.

In these methods, the vapour species of a solid material can be created either by thermal evaporation or by mechanically knocking out the atoms or molecules from the surface by using energetic heavy particles. The process of deposition in the former case is referred to as vacuum evaporation and in the later as sputtering. The thermal melting and consequent evaporation of the material to form films on the substrate is effected by various methods such as (i) resistive heating (ii) arc evaporation (iii) flash evaporation (iv) exploding wire technique (v) electron bombardment heating (vi) laser evaporation and (vii) RF or induction heating.

The ions for sputtering may be produced either by establishing a glow discharge between the target and the substrate holder or by using a separate ion-beam source. In this process ions formed in a glow discharge are accelerated to impinge on the target material. The momentum transfer between the impinging ions and the atoms of the target enables the target atom to be released. These knocked off atoms condense on a substrate to form a thin film. Adherence of the sputtered film is usually better than that of an evaporated film [2]. Since sputtering can

be done by using large area targets, film thickness uniformity over the substrate can easily be achieved. Disadvantages of sputtering include generally lower deposition rates and the requirement of more accurate pressure control during processing.

To select the best method for depositing a thin film, it is necessary to examine the characteristics of the materials. The functional properties of the thin film must also be considered together with the factors that control these properties. Desirable properties of thin films may be categorized according to the application e.g., optical, electrical, physical or chemical.

2.3 Deposition technique

Vacuum evaporation is one of the widely used deposition techniques. As the name implies, the technique consists of vapourisation of the solid material by heating it to sufficiently high temperatures and condensing it onto a substrate to form a film. Heating of the material can be carried out directly or indirectly (via a support) by a variety of methods. The simplest and the most common method is to support the material in a filament basket or boat which is heated electrically.

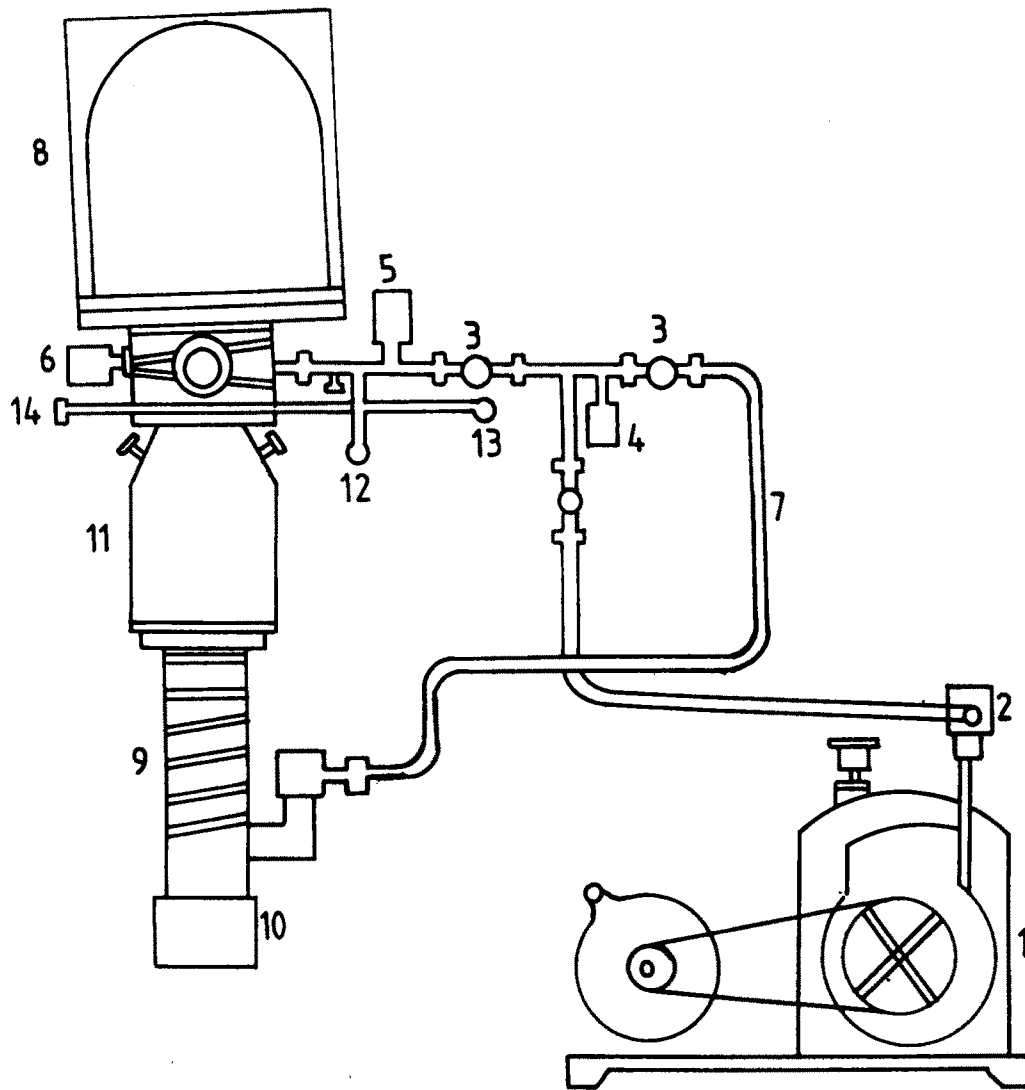
In the present work vacuum evaporation technique was used for the preparation of Sb_2Se_3 chalcogenide semiconducting thin films. The reasons behind the selection of this technique are: the amount of impurities included in the growing layer will be minimised, the tendency to form oxides will be considerably

reduced and finally straight line propagation will occur from the source to substrate which will allow for the reproduction of finely defined patterns by the introduction of a pattern masks between the source and substrates. The pressure that is required in a vacuum system to obtain satisfactory deposition in terms of the reduction of oxides, reduction of included impurities in the deposition and the fabrication of a sharply defined pattern, is less than 1.3×10^{-2} Pa with an ideal pressure for normal evaporation work being 1.3×10^{-3} Pa.

2.3.1 Vacuum coating unit

In the present study, Sb_2Se_3 films are prepared by thermal evaporation technique using 0.3m IBP TORR vacuum evaporation unit (model EPR-002). The schematic diagram of the coating unit is shown in Fig. 2.1.

The 'IBP TORR EPR-002' unit comprises of three main sections, namely (1) vacuum chamber, (2) pumping system and (3) electrical equipments with connections. The vacuum chamber is evacuated by a three stage oil diffusion pump of speed 500 liters/sec. It is backed by a double stage gas ballast rotary pump with evacuating capacity of 200 liters per minute and a liquid nitrogen trap to prevent back streaming of oil vapours. A magnetic isolation cum air admittance valve is fitted in the line in between the diffusion pump and the rotary pump to prevent back suction from rotary pump to diffusion pump due to power failure. DC 704 silicone fluid, having low vapour pressure 1.3×10^{-5} Pa,



- | | |
|-----------------------------|-----------------------------|
| 1- ROTARY PUMP | 8 - GLASS OR METAL BELL JAR |
| 2- MAGNETIC ISOLATION VALVE | 9 - DIFFUSION PUMP |
| 3- BUTTERFLY VALVE | 10- DIFFUSION PUMP HEATER |
| 4- PIRANI GAUGE I | 11- LIQUID AIR TRAP |
| 5- PIRANI GAUGE II | 12- AIR ADMITTANCE VALVE |
| 6- PENNING GAUGE | 13- NEEDLE VALVE |
| 7- BACKING LINE | 14- BAFFLE VALVE |

Fig 2.1 SCHEMATIC REPRESENTATION OF VACUUM COATING UNIT

is used as the charge for the diffusion pump. The pressure inside the chamber is measured with a thermal conductivity gauge - Pirani gauge, for low vacuum ($66.5-1.3 \times 10^{-1}$ Pa) and with an ionisation gauge, Penning gauge, for high vacuum ($1.3 - 1.3 \times 10^{-4}$ Pa). A high voltage transformer capable of delivering 500 V at 500 mA is incorporated for ion beam cleaning. A low voltage transformer capable of supplying 150 amperes at 20 volts is used to provide the necessary current for heating the tungsten or molybdenum sources which are used for evaporation purposes. copper - constantan thermocouple has been used to measure the temperature of the substrate during deposition. In order to remove the surface impurities, the evaporant sources were pre-cleaned by heating them at higher temperature with the shutter closed. Prior to each evaporation the evaporant materials were carefully degassed at lower temperature for about 30 minutes. The rate of evaporation was properly controlled and has been maintained constant using a quartz crystal thickness monitor.

2.4 Bulk Sb_2Se_3 preparation

The bulk Sb_2Se_3 was prepared by taking Sb and Se (purity 99.999%, Balzers) in their atomic percentages and melting them in an evacuated quartz ampoule. The melting point of the compound (850 K) and the furnace temperature (1220 K) were fixed using the phase diagram of Sb-Se system (Fig. 2.2). The ampoule with the material was evacuated to 1.3×10^{-3} Pa and sealed. The synthesis of the compound was carried out by placing the quartz tube in

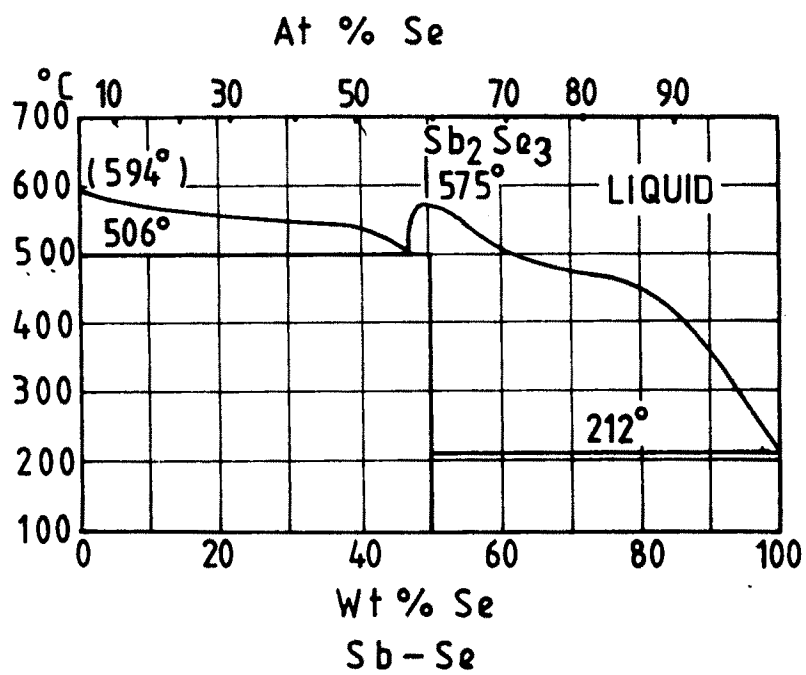


Fig 2.2 PHASE DIAGRAM OF Sb-Se SYSTEM

a rotating furnace[3] maintained at 1220 K for 18 hours (Fig2.3).

During the course of the heating the quartz ampoule was rotated continuously to ensure homogeneity and to promote escape of any dissolved or sorbed gases in the molten mixture. The quartz tube was then quenched in the cold water bath. The resulting bulk Sb_2Se_3 was made into small pieces, suitable for thermal evaporation.

2.5 Selection of substrates

The properties of films deposited are very greatly influenced by the nature and surface finish of the substrate. The substrate should provide only mechanical support but not interact with the film except for sufficient adhesion. Also the substrate must be amenable to moderately high temperature predeposition treatments. Besides, it has to be chemically stable and comparatively cheap. Upon investigation it has been found qualitatively that glass has got maximum surface smoothness [4]. Also it is optically plane [5,6] easily available and low cost. So in the present study glass slides of $1 \times 10^{-3}\text{m}$ thickness have been used as substrates to support thin films.

A thoroughly cleaned substrate is a prerequisite for the preparation of films with reproducible properties. So, great care has been taken to clean the substrate. Cleaning involves removal of contaminants without damage to the substrates. The usual contaminants are lint residues, finger prints, oil and air

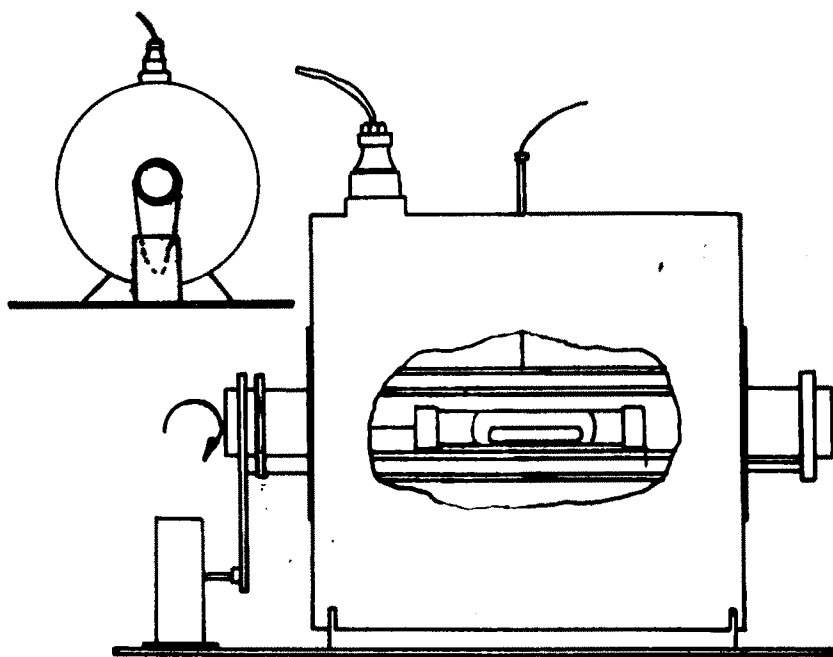


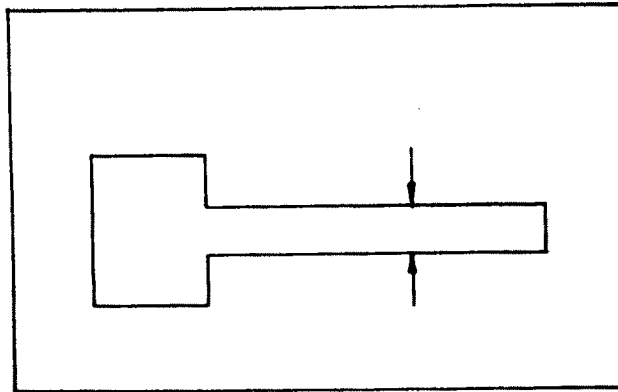
Fig 2.3 ROTATING FURNACE

borne materials. The energy required to break the adsorption bonds could be supplied by chemical solution, ion bombardment, thermal or mechanical process. The procedure adapted in the present study to clean the glass substrates is as follows.

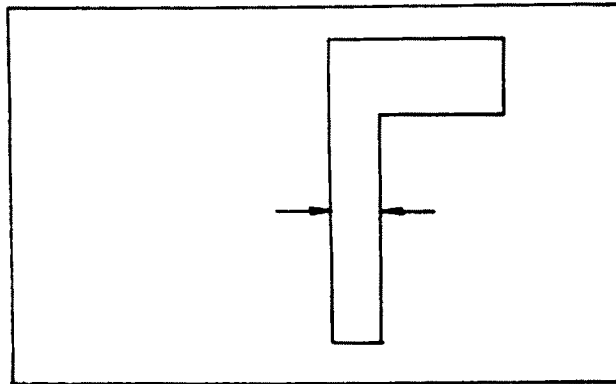
Initially, the substrates were immersed in a dilute solution of NaOH for one hour, to remove any traces of dirt and to dissolve any fatty materials. They were then cleaned with detergent solution and washed thoroughly in running distilled water. Further the glass substrates were subjected to ultrasonic agitation for about 45 minutes in distilled water mixed with some drops of detergent solution. The shock waves created in the solvent rendered possible for the removal of residues. Then the substrates were vapour degreased with pure isopropanol. The system was rigged up such that the rising vapours of the solvent on the substrates thereby heating them and increasing the rate of dissolution of surface contaminants. As the spent solution drips back into the bath, fresh and clean distillate repeat the process. The substrates were then baked in an oven at about 420 K for one hour.

2.6 Masks and MSM structures

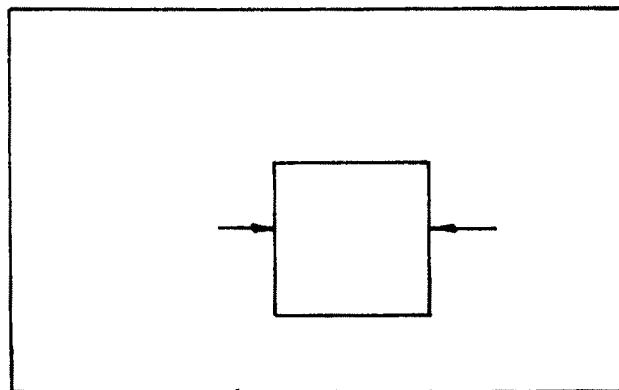
Suitable masks have been used to form the desired pattern for various studies (Fig. 2.4). The brass masks of precise dimensions (Fig. 2.4) with vertical edges have been prepared by the photolithographic technique [7]. All the masks have to be cleaned prior to use since dust particles, fibers or debris from



$2 \times 10^{-3} \text{ m}$



$2 \times 10^{-3} \text{ m}$



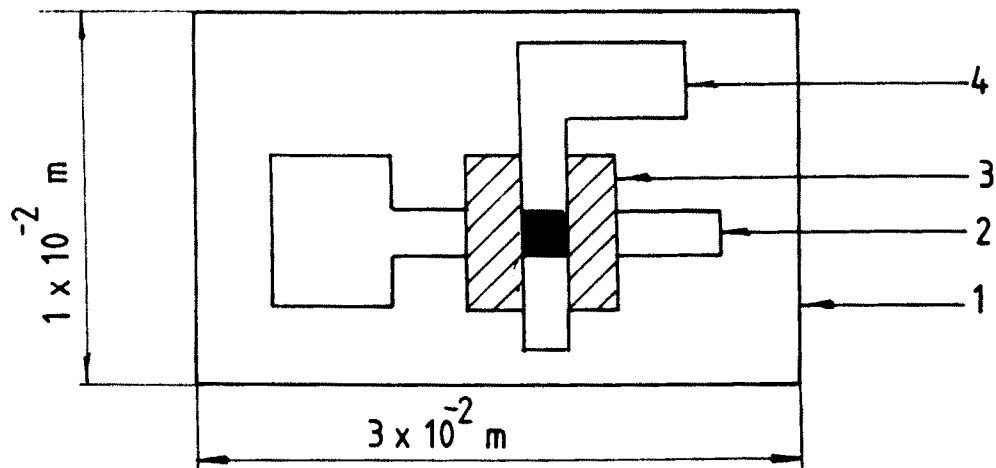
$4 \times 10^{-3} \text{ m}$

Fig 2.4 MASKS USED TO FORM MSM STRUCTURE

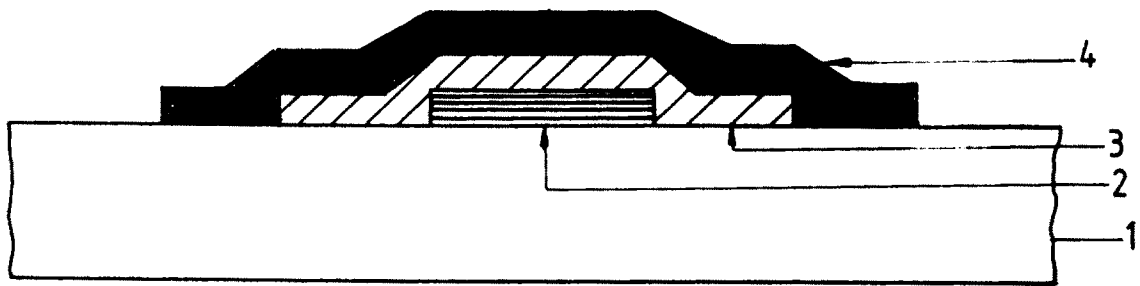
machining process may cause discontinuities in the deposited film pattern. The masks were cleaned with acetone and then heated in an oven at about 420 K for 30 minutes. Again these masks were ultrasonically agitated in distilled water and dried before making use of them.

Metal-semiconductor-metal (MSM) sandwich structures were formed (Fig. 2.5) onto glass substrates with the semiconducting layer in between two metal electrodes by using suitable masks. The electrode material should be such that it should not react with the dielectric film and should have a low electrical resistance and good adhesion to the substrate. Generally metals like gold, silver, copper and aluminium have been used as electrode materials. Aluminium, high pure with low cost, has been established to possess both the qualities and therefore has been used for electrode deposition in the present study.

Pure aluminium (99.99 %, Balzers) was evaporated at a pressure of 2.6×10^{-3} Pa from a helical tungsten filament by resistive heating onto well cleaned glass substrates through suitable masks to form the base electrode. The source to substrate distance was maintained as 0.18m. Then Sb_2Se_3 film has been deposited through an appropriate mask by vacuum evaporation technique. Finally upper electrode was formed by again evaporating the aluminium so as to form MSM structure.



■ ELECTRODE OVERLAPPING AREA(A)



- | | |
|--------------------|-----------------------|
| 1 SUBSTRATE | 3 SEMICONDUCTING FILM |
| 2 BOTTOM ELECTRODE | 4 TOP ELECTRODE |

Fig 2.5 MSM SANDWICH STRUCTURE AND ITS VERTICAL CROSS SECTIONAL VIEW

2.7 Substrate heater and temperature measurement

For the preparation of polycrystalline thin films, during deposition the substrates should be kept at higher temperature and a special substrate holder designed for the above purpose.

The substrate heater comprises of a nichrome strip wound over a thick mica sheet, in an annular ring shape, sandwiched between two thin mica sheets and a pair of thick metal plates. The mica sheets placed on both sides of the heating element is sandwiched between the two metal plates. These two metal plates have an inner diameter of 0.05m and an outer diameter of 0.25m. The substrates are held against the heater surface with proper clamps. With this heater, an area of 0.047m^2 can be uniformly heated to within $\pm 2^\circ\text{C}$ with the temperature controller. The temperature of the substrate was measured by a copper-constantan thermocouple which was kept in contact with the surface of the substrate exposed for deposition. On the whole 15 substrates can be accommodated out of which 12 are of the size $1.0 \times 10^{-2} \times 3.0 \times 10^{-2}\text{m}$ and the remaining three are of $1.0 \times 10^{-2} \times 1.0 \times 10^{-2}\text{m}$ size. In one pumping cycle 15 substrates of three different thickness have been prepared using the substrate holder.

2.8 Thickness measurement

Among the most significant thin film parameters, thickness of the deposited thin film plays a vital role. The commonly

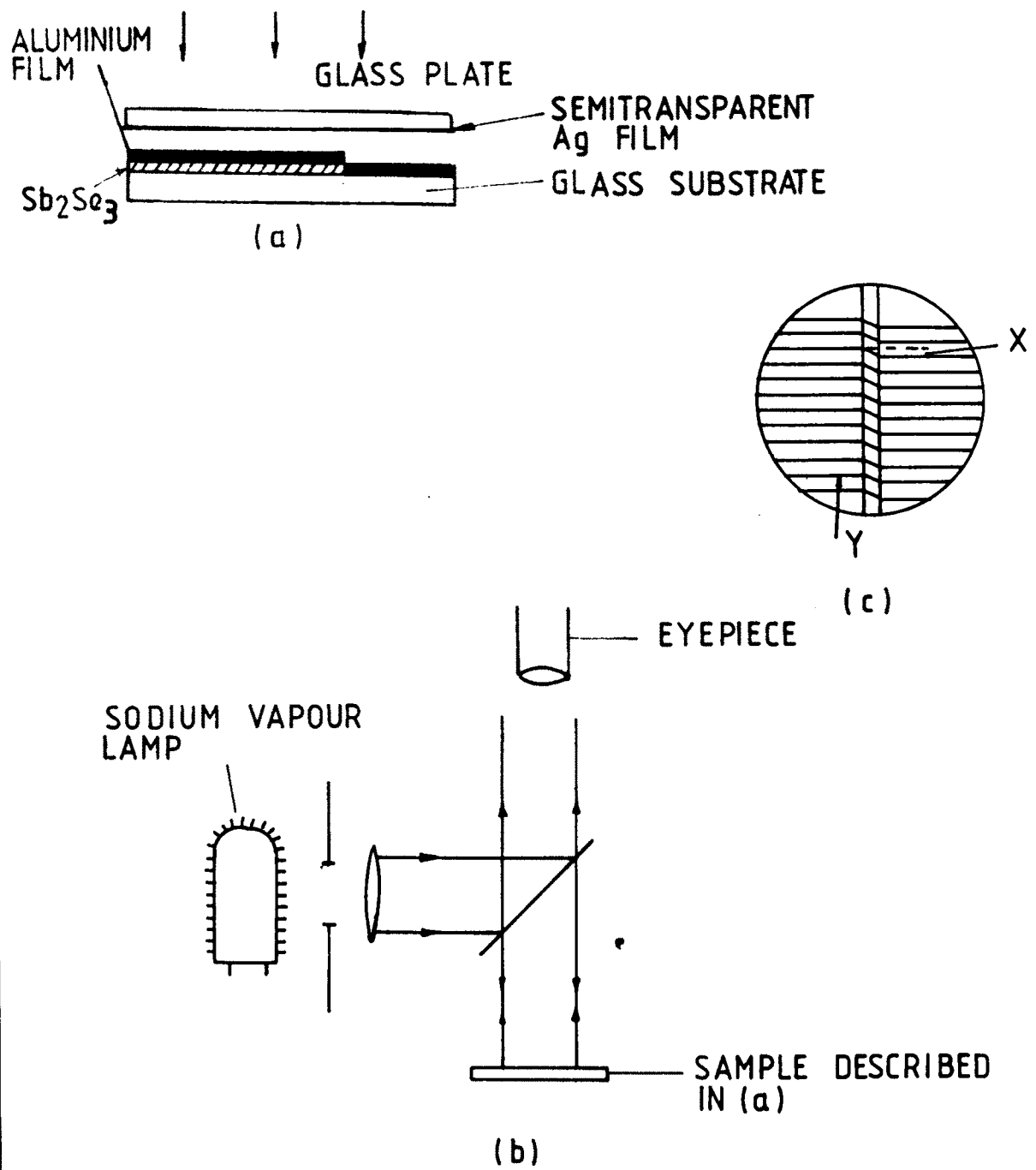
employed methods for thickness measurement are classified into five categories [8-13] viz., (i) mechanical method (ii) microbalance (iii) crystal oscillator (iv) radiation (v) ionisation and (vi) optical methods. Optical methods are further classified into different categories viz., Optical monitor, polarimetric and interferometric methods. In the present study both interferometric and crystal oscillator techniques were used to determine the film thickness.

2.8.1 Multiple beam interferometric (MBI) method

The thickness of the film was measured using Tolansky's interference method [11-14]. The technique consists of a reflecting film like silver over the Sb_2Se_3 film in such a way to form a mechanical step as shown in Fig 2.6(a). A glass plate coated with a semitransparent silver film was held as shown in the Fig. 2.6(a) and the step was viewed through a comparator. The experimental setup is illustrated in Fig. 2.6(b). An interference pattern as shown in Fig. 2.6(c) is obtained in the field of view of the comparator. The discontinuity in the fringe pattern is clearly due to the step whose height is identified with the thickness of the Sb_2Se_3 film and is given by the relation,

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

where x and y are the measured quantities as indicated in Fig. 2.6(c). Normally sodium vapour lamp of wavelength 589.3nm



(a) SAMPLE ARRANGEMENT
 (b) EXPERIMENTAL SET-UP
 (c) TYPICAL FRINGE PATTERN OBSERVED

Fig 2.6 MULTIPLE BEAM INTERFEROMETRY FOR THICKNESS MEASUREMENT OF ITO FILM

is used as the monochromatic source. The comparator used in this case has a least count of $0.0001 \times 10^{-2}\text{m}$. In the present work, the lowest measured thickness of the Sb_2Se_3 films measured by this technique is about 100 nm.

2.8.2 Quartz crystal thickness monitor

The use of quartz-crystal oscillators to determine small quantities of deposited matter was first explored by Sauerbrey [5,16] and Lostis [17]. The transducers required to monitor film thickness are of simple construction and are unaffected by mechanical shocks and external vibration. The crystal-oscillator monitor utilizes the piezoelectric properties of quartz. A thin quartz crystal wafer with gold electrodes on its two surfaces is incorporated into an oscillator circuit of fixed radio frequency generator. This wafer is installed in a vacuum coating system so that one surface is exposed to the evaporation source. The coating deposited on the crystal surface loads the crystal and changes the oscillating frequency.

The quartz crystal thickness monitor (Hind HIVAC, Model CFM1) used in the present study consists of a monitor crystal (6.0MHz) positioned in the vacuum chamber in such a way that the same thickness of the film is deposited both on the substrate and on a defined area of the crystal surface. A second crystal (6.5MHz) the reference crystal is mounted in the control unit outside the vacuum chamber. The monitor and reference crystals are AT cut quartz crystal oscillating in a fundamental thickness shear mode.

AT cut crystals are used because of their higher effective mass sensitivity.

The difference between the crystal frequencies is amplified, fed into another circuit where it is mixed with a variable oscillator to produce a final difference in frequency between 0 and 100 KHz. The mass of the deposited material (the thin film) causes a reduction in the natural resonant frequency of the monitor crystal with the result an increase in the final difference in frequency. This change is converted into a dc signal which actuates both the frequency shift meter and the rate of change meter (the rate meter). Thus both the thickness of the film and its rate of deposition on the crystal face are displayed on conventional meters. At the end of one deposition the substrate is changed and the frequency shift meter rests to zero by manual adjustment of the variable oscillator. Rate of deposition is indicated in Hertz/second by a diode pumping type frequency to voltage converter and through a differentiating circuit.

2.8.3 Calibration

To determine the film thickness over a wide range, the films of varying thickness are prepared overlapping the required range at both ends. Each film thickness is measured by a multiple beam interferometer and the results are plotted on a graph with film thickness against the frequency change. This linear graph was then used to measure the film thickness from frequency shift in the range covered.

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