CHAPTER – 5

EXPERIMENTAL TECHNIQUES

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Various techniques employed in the investigations during the course of work are described briefly in this chapter together with some alternative allied techniques which may also be used. These include Bridgman- Stockbarger[1] and Zone Melting[2] crystal growth methods, X-ray diffraction, dislocation etching, preparation of thin films and measurement techniques of optical and electrical properties, surface observation etc.

TECHINEQUES FOR CRYSTAL GROWTH :

Synthesizing the compound :

To obtain a homogeneous mixture of the weighed proportions of the components of the alloys, a melt – stirring method was used. It consists of a resistance furnace with a cylindrical core of about 45 cm in length and 5 cm in diameter. A ceramic tube of 60 cm in length and 1.5 cm in diameter is passed through the cylindrical core. A uniform temperature zone of about 10 – 12 cm length is obtained inside this tube. The two ends of the tube are fitted to two brass sockets. The sockets are pivoted on frictionless bearings for smooth motion without wobbling. The tube is rotated at 10 r.p.m. by an electrical motor. A photograph of the

mixing unit is given in figure-1. A quartz ampoule evacuated to about 10^{-4} Pa pressure and containing the charge is sealed and inserted in the ceramic tube for melting and stirring the charge. The maximum temperature inside the furnace core is kept about 100 ^{0}C above the melting point of the material. The temperature is measured and controlled (within $\pm$ 5 ^{0}C) with a proportional temperature controller. The temperature is sensed with a chromel-alumel thermocouple. The rotation cum rocking of the quartz tube gives stirring effect to the molten charge. For thorough mixing and reaction of the charge, this treatment is continued for 2 to 3 days. The molten charge is then slowly cooled to room temperature.

Bridgman-Stockbarger method :

Bridgman – Stockbarger technique is capable of producing large size crystals from thin rods to ingots of several cm in diameter. The Bridgman crucible is usually a tube of circular cross section with a tapered shape formed at one of the ends. The tapered end leads through the negative temperature gradient thereby effecting the charge transform from liquid to solid state and it provides conditions for single nucleation event required to grow subsequently as a single crystal through the rest of the material as it solidifies. The Bridgman-Stockbarger vertical furnace is divided into two halves, the temperature of which can be varied

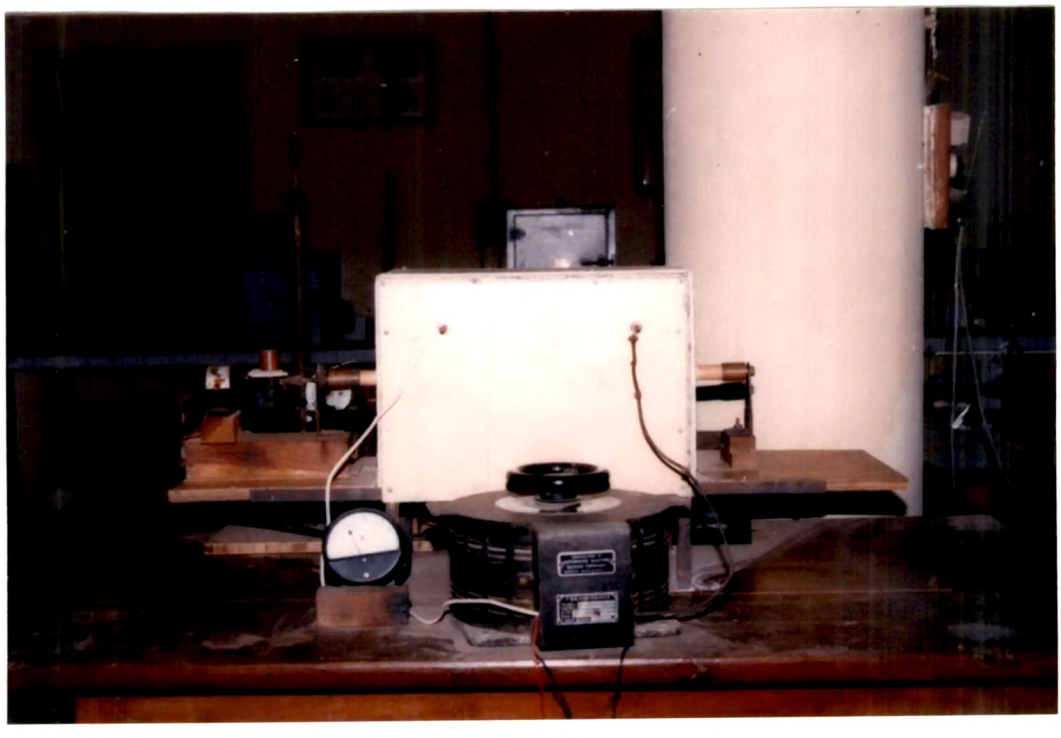

Fig. 1

independently and hence suitable temperature gradient can be obtained. The apparatus consists of a vertical resistance furnace having a cylindrical core 55 cm in length and 5 cm in diameter, prepared in the usual way. It is properly lagged to avoid radiation losses. The temperature of the furnace is controlled ($\pm$ 5 ^{0}C) using a chromel-alumel thermocouple and a temperature controller. The temperature gradient in the furnace in the region of interest, viz, the lower end wherethrough the molten charge is lowered for unidirectional solidification, could be varied in the range from about 35 ^{0}C/cm to 45 ^{0}C/cm. The ampoule containing the charge is sealed at 10^{-4} Pa pressure and is kept at the center of the furnace. The central temperature is maintained 50 ^{0}C above the melting point for a sufficient time to melt the complete charge and then it was lowered down the furnace. The lowering is facilitated by a gear mechanism coupled with a 0.5 H.P. motor. The lowering speed could be varied from 0.35 cm/hr to 1.0 cm/hr by changing the output shaft of the gears. A photograph of the unit is shown in Figure - 2.

Zone melting method :

The apparatus consists of a long quartz tube of about 100 cm in length and 2 cm in diameter. A ring or zone furnace is mounted on a trolley and the tube is passed through the furnace and clamped at its two ends. The motion of the furnace on trolley is controlled by a gear mechanism connected with a 0.5 H.P. motor. A photograph of the unit is

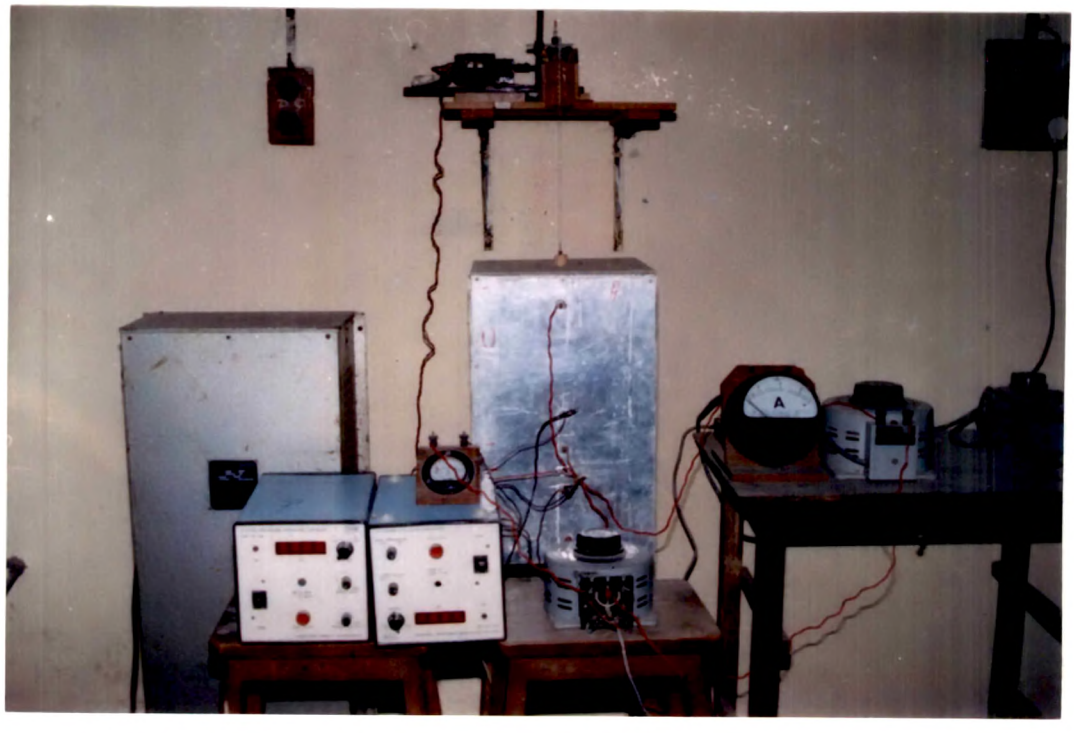

Fig. 2

shown in Figure - 3. The vacuum sealed quartz tube containing the charge was then kept inside the long quartz tube. At a maximum temperature of 180 ^{0}C in the furnace, an appropriate temperature gradient, viz, of about 30 ^{0}C/cm is obtainable at both the solid-liquid interfaces using this furnace. The detailed growth of $InBi_{1-x}Sb_x$ and $InBi_{1-x}Se_x$ single crystals by this apparatus is discussed in chapter 6.

The single crystalline character of the crystals thus grown was asserted by

(1) Cleavage test and

(2) Etching test.

The smoothness and hence the perfection of cleavage plane depends on the quality of the crystal grown. This can further be confirmed by etching the surface in a dislocation etchant and examining the distribution and shape of each of each pits.

OPTICAL MICROSCOPY :

Vickers microscope :

The microtopographical study of the crystal surface was carried out using the Vickers projection microscope. It is an inverted metallurgical type optical microscope. For examination of the crystals, this microscope carries two different systems. One of them is the transmission and the other reflection system. The present work in this

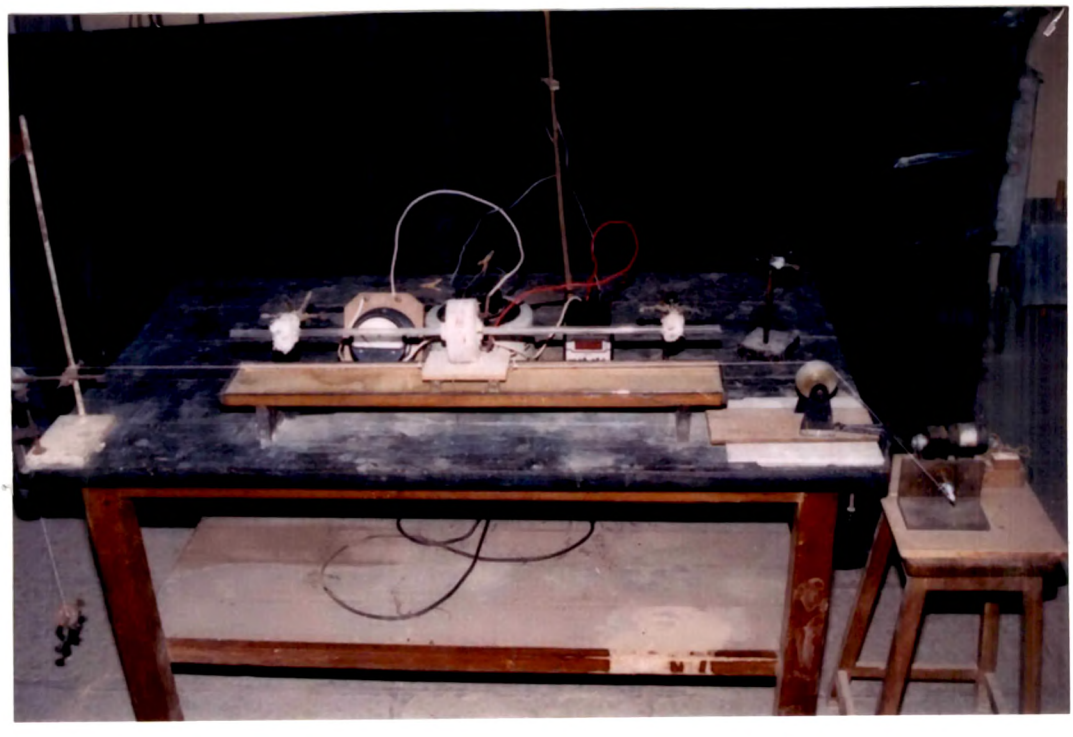

Fig. 3

thesis involves optically opaque crystals and only the reflection system was used for the purpose. This equipment also provides for phase contrast and light-profile techniques.

X-RAY POWDER DIFFRACTION TECHNIQUE :

A given substance always produces a characteristic diffraction pattern, whether that substance is present in the pure state or as one constituent of a mixture of substance. This fact is the basis for the use of diffraction method for chemical analysis. X-ray power diffraction (XRPD) techniques are used to characterize samples in the form of loose powders or aggregates of finely divided material. Qualitative analysis for particular substance is accomplished by identification of the diffraction pattern of that substance. Quantitative analysis is also possible, because the intensities of the diffraction lines due to one phase of a mixture depend on the proportion of that phase in the specimen.

The powder method is best known for its use as a phase characterization tool partly because it can routinely differentiate between phases having the same chemical composition but different crystal structure (polymorphs). As a result, the diffraction method has been widely applied for the materials analysis.

In the XRPD technique, the powder sample is placed in a collimated monochromatic beam of X-radiation. The technique usually

requires some sample preparation. This may involve crushing the sample to fit inside a glass capillary tube, rolling it into a very thin rod shape for the Debye-Scherrer camera technique, spreading it as a thin layer on a sample holder or packing it into a sample holder of a certain size. In some cases, the preparation would depend on the equipment available and the nature of examination. A diffraction pattern can be recorded on a photographic film, or by use of analog or digital methods. In any case, the final data can be displayed as a graph of intensity as a function of interplanar distance d, or as a function of diffraction angle 2θ. Many modern automated powder diffractometer can provide further data reduction, including peak finding a tabular listing of peak intensity versus interplanar spacing employing search / match software and other computer utilities.

Phase identification using XRPD is based on the unique pattern produced by every crystalline phase. Much as a fingerprint is unique for each person, the diffraction pattern can act as an empirical fingerprint for that phase and qualitative identification of phase can be accomplished by pattern-recognition methods that include established manual techniques and the newer method that use computers, most of which implement programs based on heuristic algorithms. All of these methods make use of the database maintained by the JCPDS international centre of Diffraction Data[3]

There are two different designs of diffractometer used for obtaining XRD pattern of powder samples and thin films.

The first one is "The Bragg-Brentano X –ray diffractometer". Here the specimen is mounted in the centre of the diffractometer and rotated by an angle θ around an axis in the film plane. The counter is attached to an arm rotating around the specimen axis by angle twice as large as those of the specimen rotation. Only (hkl) planes parallel to the film plane contributes to the diffraction intensity. The effective thickness of a film 't' decreases with increasing diffraction angle. Therefore the effective thickness of a film in 100 nm thickness range is sufficient to excite measurable diffracted radiation at small angles but the intensity falls off rapidly for higher index reflections.

The second design of diffractometer utilizes the Seeman-Bohlin effect, in which the specimen and focussing circle remain stationary, while the detector tube moves along the circumference of the focussing circle itself. Its main advantage is the constant angle of incidence, which can be kept as small as 5^0, thus giving higher diffracted intensities than those obtained by Bragg-Brentano diffractometer in the whole angular range and particularly in the reflection region. However, in the present case diffractometer based on Bragg effect is used.

MICROHARDNESS TEST :

The Vickers microhardness was measured using Vickers diamond indenter [supplied by M/s. Cooke Toughton and Simms Ltd., England] which can be used with the Vickers projection microscope (Fig. 4). The indenter is in the form of a square pyramid with semi apex angle = 68^0. All the instructions suggested by the supplier were rigidly observed. Since there is no provisions for making indentations at high temperature in the above equipment, a special arrangement described below was attached to the hardness testing jig.

A cylindrical shape refractory block [Fig. 5] was used to mount the specimen. The diameter and length of this block being such that it can easily be fitted in the collet of the hardness-testing unit of the microscope. A small heating element was passed though this mount. A circular brass disc of the same diameter as the mount was fitted on the top of this mount. The specimen can be fitted on this disc by a proper adhesive. A copper constantan thermocouple was placed through a groove 1 mm below the top of the brass disc. Known melting points of some substances like paraffin wax, Indium metal, InBi, Tin etc., were checked to calibrate this heating arrangement. The error in any case did not exceed 2 ^{0}C. Before indenting the specimen, care was taken to get thermal equilibrium.

The Vickers hardness H_v, was calculated using the formula,

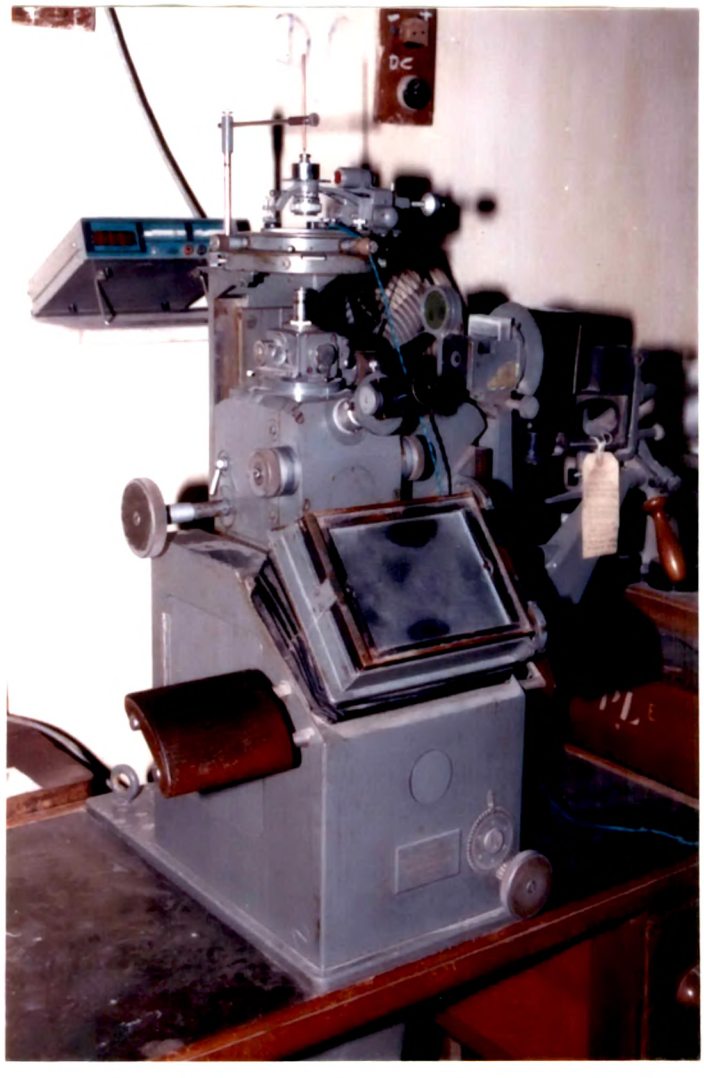

Fig. 4

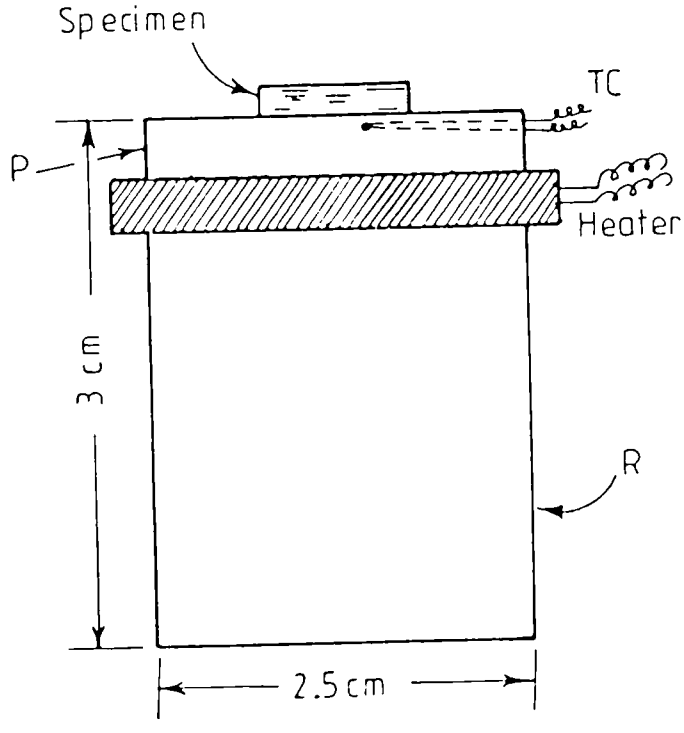

Fig. 5

$$H_v = \frac{1854 \times P}{d^2} \quad Kg/mm^2 = \frac{1854 \times P}{d^2} \times 9.8\ MPa$$

in accordance with the definition given by Cooke, Toughton et al[4], where, P is load in gram and d is the average diagonal length of indentation mark in microns. To measure the diagonal of the indentation mark, a micrometer eyepiece with the least count 0.19 micron was used.

EXPERIMENT SET UP FOR THIN FILM GROWTH :

Vacuum Coating System :

In the present work, for the thin film deposition "Hind Hivac" vacuum coating unit, Model No 12 A – 4 (Figure - 6) was used. The chamber material is polished stainless steel with vacuum sealed glass windows for visual inspection of the coating process. A Pyrex glass bell-jar is also provided. The system consists of a double stage gas ballast rotary pump having a capacity of 200 lit./min. and an oil diffusion pump OD-114 having oil charge of 150 to 200 cc. The rotary pump is connected with a moisture trap mounted directly above the inlet of the pump. A tray containing the dessicant in the form of pellets (usually activated alumina) is kept inside the trap body. The gases passing through this trap come in contact with the dessicant which absorbs the water vapour present in the gas. This avoids contamination of the rotary pump oil with water and other harmful vapours.

Fig. 6

To isolate the vacuum chamber from the pump it is provided with a solenoid valve to admit the air automatically into the rotary pump either on switching off the system or on failure of electric power supply, thus giving a complete protection against the oil being sucked back.

To avoid the back streaming and hence contamination and loss of pump fluid the diffusion pump is connected with a water-cooled baffle valve which enables a working vapour pump to be isolated while the pumping system is at atmospheric pressure. A liquid nitrogen trap is also connected with the diffusion pump to avoid the back streaming and increase the action of diffusion pump.

The L.T. supply for filaments or boats is obtained from a 230V input transformer by means of series or parallel connection in the secondary of the transformer. The L.T. output of the transformer is fed through a current meter and a sector switch to L.T. leads and filament holders. It is also provided with H.T. power supply for glow discharge cleaning (ion bombardment), obtained from a high reactance transformer rated at 3.5 KV, 50 mA and 5 KV AC open circuit. A solid state power pack having a DC output is provided for H.T. cleaning and cathode sputtering supply.

Fully stabilized vacuum gauges are provided : two Pirani gauge heads one of which is mounted on the mouth of the rotary pump and the other in the chamber which can measure from 5 Pa to 10^{-2} Pa and a

Penning gauge fitted with the chamber and measuring from 10^{-1} Pa to 10^{-5} Pa.

Chamber Arrangement :

The chamber gadgetary comprises of work holder ring, which has a useful diameter of 8". A D.C. high tension discharge cleaning system consists of pure aluminium annular ring suitably shielded to avoid electron contamination of the work-piece. A source shutter swings over the source position and is operated by an external lever. A standard filament holder is fitted to the L.T. live electrode and earth electrode. The filament is normally positioned vertically below the center of the work holder to give uniform distribution of vapours. For flash evaporation a feeder with the material mesh and a conical spout is used. The alignment of the cone is above the boat. A stainless steel wire mesh is fitted over the base plate to prevent foreign bodies falling into baffle valve.

Rotary Drive:

The rotary drive is useful for uniform deposition of materials on large plane surface substrates. This consists of work holder of 6 inches in diameter and is rotated by a variable speed electric motor situated outside the chamber, without vibration. The speed is controlled by a solid state speed control.

Radiant Heater :

A radiant heater is fixed inside the chamber on the top of the work holder ring. This is capable of treating the substrate or deposited films up to a temperature 25 ^{0}C to 275 ^{0}C in about 30 minuets. Temperature measurement is done using a Chromel – Alumel thermocouple in conjunction with a digital millivoltmeter.

Thickness Measurement :

Thickness is the most significant film parameter. It may be measured either by in-situ monitoring of the rate of deposition or after the film is taken out of the deposition chamber. Usually for in-situ thickness measurement a quartz crystals monitor is used. It can be used for monitoring and controlling the rates of deposition of both metals and non-metals. The thickness measurement was obtained with an accuracy of $\pm$ 25 Å. The monitor utilizes thickness shear mode of a piezoelectric quartz crystal. Here the major crystal surfaces are antinodal and mass added on either one or both sides shifts the resonance frequency irrespective of the thickness, density, elastic constants or stiffness of the added material. The thickness of deposited film is obtained by the formula[5].

$$T = df / C_f r \text{ (film)}$$

where df is the frequency shift, C_f is a constant, characteristic of the crystal and r is film material density.

Quartz crystal thickness monitor is mounted inside the chamber above the work-holder. Water-cooling is essential when the coating is done at higher temperatures. Normally, the first layer coated on the crystal is that of aluminium to facilitate the cleaning of the crystal in case of lower activity or failure of oscillation of the crystal, by dissolving Al in NaOH. In the latter case two reflecting surfaces are brought in close proximity such that a small wedge with a small air gap in between them is formed. If a monochromatic light is now incident on them at normal incidence, then an interference of light due to interactions of multiple reflected beam in air gap will take place resulting in a series of fringes (Fizeau) which can be observed in the back reflected light. The distance between the fringes or lines depends on the air gap as well as on the wavelength of the monochromatic light. This principle is adopted and suitably modified for the multiple beam interferometric method of the measurement of film thickness[6].

A film, the thickness of which is to be determined, is deposited on a flat surface so as to leave a sharp edge between the film and the uncoated region of the substrate. An optical flat is preferred as a substrate and often a good microscopic glass slide is good enough for this purpose. The substrate with a coating of the film is then given a heavy and highly reflecting coating of a metal such as silver or aluminum so as to form a sharp step on the film edge. Another flat (optically) glass slide known as

the reference plate, with a partially transparent film of the same metal, is then placed over the specimen with their metal coated surfaces in contact with each other so as to leave a small air gap at the step. A monochromatic parallel beam of light passing through a beam splitter or a glass plate inclined at 45^0 is then incident on the two plate assembly and reflected light is then observed through a microscope (Figure - 7). A set of sharp fringes perpendicular to the step with equal displacement will be observed and the thickness (t) can be determined using the relation[7].

Thickness of thin film $t = \frac{b\lambda}{2a}$

where ,

b = Displacement of the fringes at the step

a = Distance between consecutive fringes and

λ = Wave length of light used.

= 5893Å (Sodium Vapour Lamp).

These fringe displacements which are in the form of parallel lines, however, occur at film edge. The sharpness of fringes depends on the reflectivity of the metal coating, the spread of the incident beam, air gap etc. It is also essential that the metal coating on the two plates, viz., the substrate and the reference plate should be of the same material since a phase change occurs when a beam of light is incident in each of the metal coating. This technique is capable of resolution of about 10Å. This is one of the simplest methods, which can be adopted for measurement of

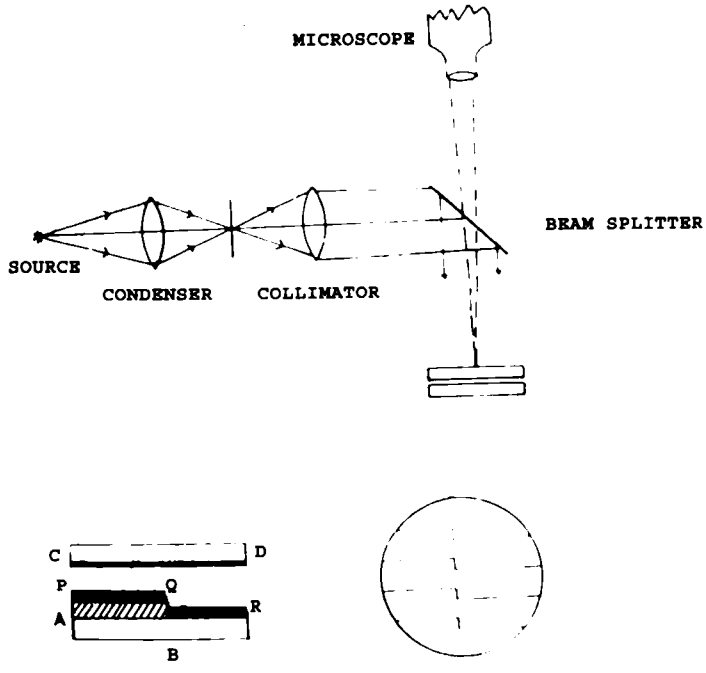
MICROSCOPE
BEAM SPLITTER
SOURCE
CONDENSER
COLLIMATOR
C
D
P
Q
A
R
B

Fig. 7

thickness varying say from 30Å to 20,000Å. This is the only property – independent method for t measurement.

In the present work the thin films of $InBi_{1-x}Sb_x$ and $InBi_{1-x}Se_x$, of different thicknesses were deposited on glass substrates at 10^{-4} Pa pressure. The thickness of these films was measured by multiple beam interferometry using the above equation.

THE SPECTROPHOTOMETER :

The spectrometer is a self-contained unit consisting of one sample compartment and a sealed interferometer compartment. The sample compartment is enclosed in a purge cover provided with access doors. Mirrors are used to channel infrared radiation to the sample position and to the detector. The instrument compartment contains a stabilized infrared light source, the Michelson interferometer, and infrared – transmitting "beamsplitter", a Helium – Neon laser for measurement of scan position, power supplies and electronic assemblies. The cast aluminum compartment is sealed to prevent the entry of dust and moist air, which can erode the beamsplitter. The specifications of the instruments are listed in Table-1. There are no routine adjustments to be made on the spectrometer.

The absorbance in the range 1500nm to 20,000nm was measured using IR spectrometer [BOMEM, Canada, MB 100 (Fig - 8)]. The films

to be measured were deposited on KBr crystal substrates and were mounted on the sample holder. The instrument acquires an interferogram and transform it to a spectrum in terms of wave number. The KBr plates used were of thickness less than 1 mm. The wave number resolution of the instrument is 4 cm^{-1}. It uses Glowbar IR source and DTGS detector[9].

Table – 1

Spectrometer Specification

Source	Glowbar, high intensity and power stabilized.
Wave number precision	0.01 cm^{-1} controlled with an internal HeNe laser.
Detector	High speed Deuterrated triglycine sulfate(DTGS)
Resolution	4cm^{-1} fixed
Beam splitter	Proprietary ZnSe design
Wave number range	6000 cm^{-1} to 510 cm^{-1}

Fig. 8

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