CHAPTER - 4

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

I. TECHNIQUES FOR CRYSTAL GROWTH :

1.1 Synthesizing the compound :

To obtain a homogeneous mixture of the weighed proportions of the components of alloys, a melt-stirring method was used. It consists of a resistance furnace with a cylindrical core of about 45 cm in length and 5cm in diameter. A ceramic tube of 60 cm in length and 1.5cm in diameter is passed through the cylindrical core. A uniform temperature zone of sufficient length, depending on the maximum temperature in the furnace, 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 shown 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°C above the melting point of the material. The temperature is measured and controlled (within ± 5°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.

1.2 Crystal growth :

Crystal growth is a complex process which usually takes place by a phase change and it can broadly be categorised as follows :

1. Solid state growth : Solid-Solid phase transition.
2. Melt growth · Liquid-Solid phase transition
3. Vapour growth : Vapour-Solid phase transition

Crystallization from melt is the most widely used method for crystal growth, mainly due to the higher growth rates obtainable and because it is easily susceptiable to modifications. Also chance of chemical contamination are reduced compared to other methods All the basic techniques are variants in the way

Fig.1

materials can be crystallized in rods, crucibles, boats or tubes. Thus the Czochralski techniques involves controlled crystallization from a crucible by pulling the melt whereas the Kyropoulos techniques does not involve pulling but crystallisation onto a seed-crystal in a crucible. Zone melting is the generic term for a series of techniques in which a molten zone (or zones) is formed and traversed along a bar so as to produce progressive melting and freezing. The horizontal Bridgman method involves the progressive crystallization of molten material in a boat or tube whilst the Stockbarger (vertical Bridgman) technique is the vertical equivalent of the lateral process[3].

(1) Bridgman – Stockbarger method :

Bridgman-Stockbarger technique is capable of producing large size crystals from thin rods to ingots of several cms 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 grain through the rest of the material as it solidifies. The Stockbarger-Bridgman vertical furnace is divided into two halves, the temperatures of which can be varied independently and hence suitable temperature gradient can be obtained.

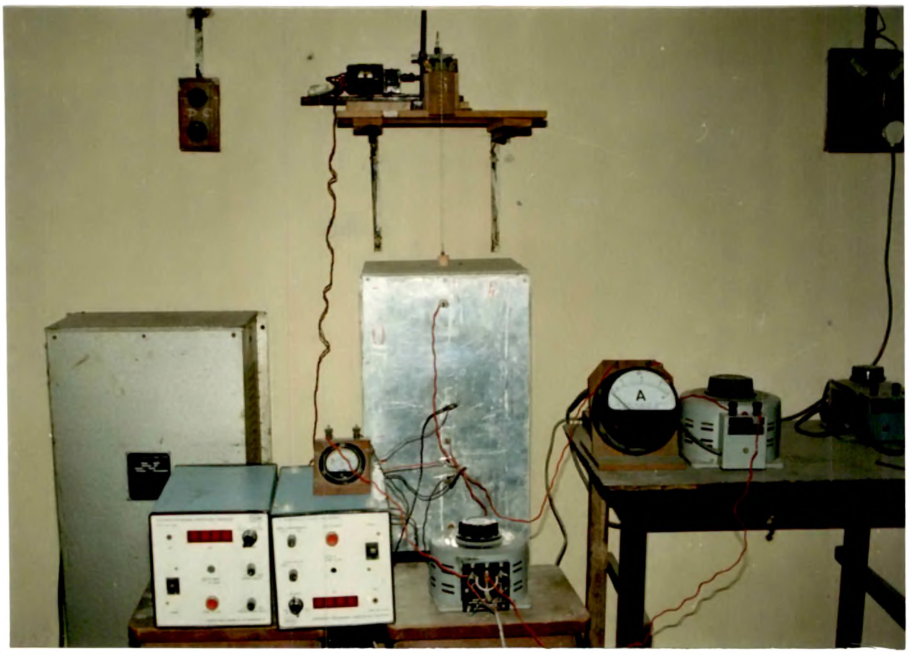


Fig.2

The apparatus consists of a vertical resistance furnace having a cylindrical core 55cm in length and 5cm in diameter, prepared in the usual way. It is properly lagged to avoid radiation losses. The temperature of the furnace is controlled (±5°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°C /cm to 45°C/cm. The ampoule containing the chrage is sealed at 10^{-4} Pa pressure and is kept at the centre of the furnace. The central temperature is maintained 50° 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 0.4cm/hr to 1.0 cm/hr by changing the output shaft of the gears. A photograph of the unit is shown in Figure-2.The detailed growth of $In_xBi_{2-x}Te_3$ (x = 0.1 to 0.5) single crystals by this method is described in chapter 6.

(2) Zone melting method :

The aparatus consists of a long quartz tube of about 100cm in length and 2cm 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 shown in Figure-3. The vacuum sealed (10^{-4}Pa) quartz tube containing the charge was then kept inside the long quartz tube. At a maximum temperature of 750°C in the furnace, an appropriate temperature gradient, viz, of about 70°C /cm is obtainable at both the solid-liquid interfaces using this furnace. The detailed growth of $In_xBi_{2-x}Te_3$ (x = 0.1 to 0.5) 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 etch pits.

II. THIN FILMS :

Modern day technology requires several types of thin film for a variety of application.The films can be single or multilayer coatings on suitable substrates of different shapes and sizes.

The basic steps involved in a thin film deposition technique are :

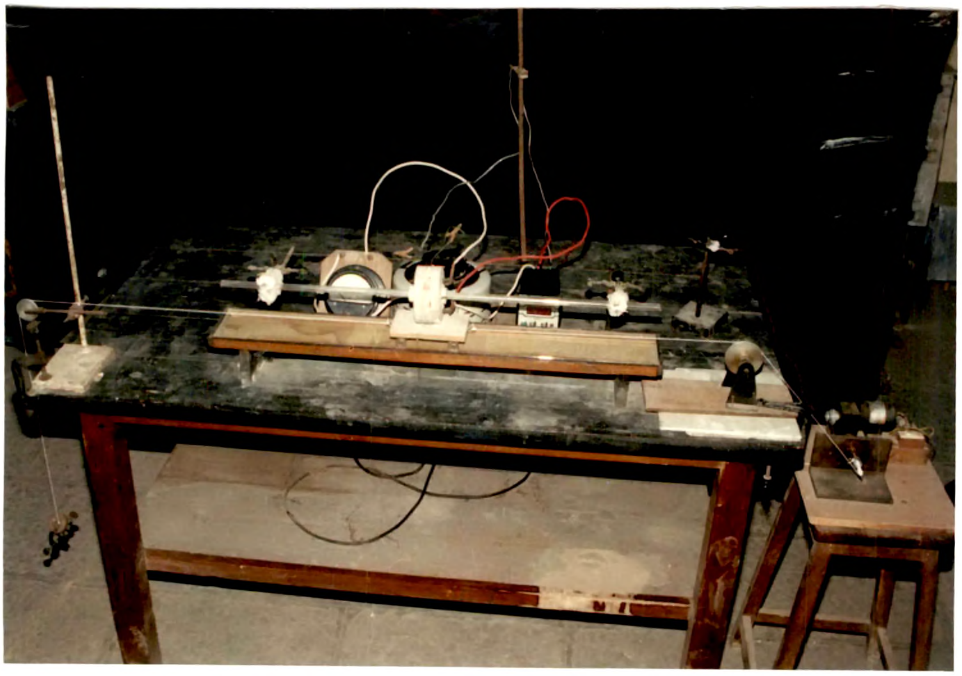


Fig. 3

(a) Creation of material to be deposited in an atomic, molecular or particulate form prior to deposition.

(b) Transport of material to the substrate in the form of a vapour stream, spray etc.

(c) Deposition of the material on the substrate and film growth by nucleation and growth process.

Thin film deposition techniques have been broadly classified into four main categories :

1. Physical Vapour Deposition (PVD)
2. Chemical Vapour Deposition (CVD)
3. Electroless or Solution growth deposition.
4. Electro Chemical Deposition (ECD).

By combining PVD and CVD, hybrid techniques such as reactive evaporation / sputtering and plasma deposition have also been developed. The PVD technique has been used in this investigation.

PVD techniques are further classified into :

(i) Thermal evaporation.

(ii) Electron beam evaporation.

(iii) Molecular beam epitaxy (MBE).

(iv) Activated Reactive evaporation (ARE).

(v) Ion plating.

2.1 THERMAL EVAPORATION :

It is one of the well known PVD techniques and the most widely used one. Large variety of materials (metals and semiconductors) can be evaporated and deposited on different substrates.

In the thermal evaporation, the material is created in a vapour form by means of resistive or RF heating. On heating a material in vacuum it evaporates at a rate given by the well known Langmuir-Dushman equation. The vapour atoms are transported through vacuum and get deposited on the substrates. Only at pressure $\leq 10^{-4}$ Pa, the mean free path of molecules becomes large so that the vapour beam reaches the substrate nearly unscattered.

A variety of sources are used to evaporate materials, depending on whether the materials are in wire, foil, ingot or powdered form. The material used as a resistive source of heat is a refractory metal like W, Mo etc. One can evaporate from two or more sources in order to deposit a multilayer film of an alloy / compound.

Direct thermal evaporation of intermetallic compounds may pose some practical difficulties. These compounds cannot be deposited without due consideration of their dissociation which may take place even below their melting points in some cases. There may arise difficuilties in growing films of stoichiometric composition from alloys and complex chemical compounds. The adhesion of film to substrate depends on the level of purity of the substrate surfaces, procedure of its cleaning and film deposition condition, etc.

In order to overcome these difficulties, the thehniques known as flash evaporation may be used It is generally used for deposition of materials whose constituents have vastly differing vapour pressures and which are known to decompose easily on vaporization . It is applicable to certain alloys, metal–dielectric mixtures and compounds. In most of the cases, vapours impiging on the substrate are highly supersaturated so that the film composition is not affected by condensation cofficients In this technique, a fine powder of the compound is sprinkled over a heated sheet/ boat, which is at a high tempurature as compared to the melting point of the compound, to produce an instantaneous and complete evaporation of the compound. The powder is kept in a feeder which is electromagnetically vibrated to let the powder drop slowly on the preheated boat.

2.2 ELECTRON BEAM EVAPORATION :

The tempreratire of the evaporant material can also be raised by electron bombardment instead of resistive heating. The thermionic electrons are accelerated through a potential of 5KV to 10 KV and focussed on the material. The electrons lose their kinetic energy mostly as heat energy and the temperature at the focal point may be raised up to about 3000°C. At such a high temperature, most of the refractory metals and compounds can be evaporated. The temperature at the focussed point is very high while rest of the material remains cool. The result is lesser interaction between the material and the support and reduced contamination. Evaporation rate can be varied by changing the input power

2.3 MOLECULAR BEAM EPITAXY (MBE) :

The deposition of single crystalline (epitaxial)films by the condensation of one or more beams of atoms and/or molecules from Knudsen (effusion) source, under UHV conditions, is called molecular beam epitaxy.

Epitaxial films of compound semiconductors like GaAs, CdTe, etc. are usualy deposited by this technique. The technique achieves precisely controlled properties of the film. The growth temperature is low, which minimizes the thermal effects like diffusion. The growth rate is also small (1 to 10Å / sec.).

2.4 ACTIVATED REACTIVE EVAPORATION :

If the evaporated material (by resistive heating or electron beam evaporation) is transported through a reactive gas plasma (oxygen, acetylene etc.), the deposition technique is known as activated reactive evaporation. It is used to deposit highly adherent films of oxides and carbides

2.5 ION PLATING :

In this process the substrate and film are exposed to a flux of high energy ions during the deposition The energy of the ion is high enough to cause changes in the interfacial region and film properties such as adhesion of the film, its morphology and density The evaporation of material is done by resistive heating or electron beam bombardment. A plasma is created in the working gas like argon either by keeping the substrate at high negative potential or by electrons emitted from a hot filament and accelerated to an anode. The negative potential at the substrate accelarates the ions to a desired energy [4]. In the present work the thermal evaporation technique has been used to grow thin films of $In_{0.1}Bi_{1.9}Te_3$, $In_{0.2}Bi_{1.8}Te_3$ and $In_{0.5}Bi_{1.5}Te_3$.

II. EXPERIMENTAL SET UP FOR THIN FILM GROWTH :

3.1 Vacuum Coating System :

In the present work, for the thin film deposition. 'Hind Hivac' vacuum coating unit, Model No.12 A-4 (Figure-4) 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.

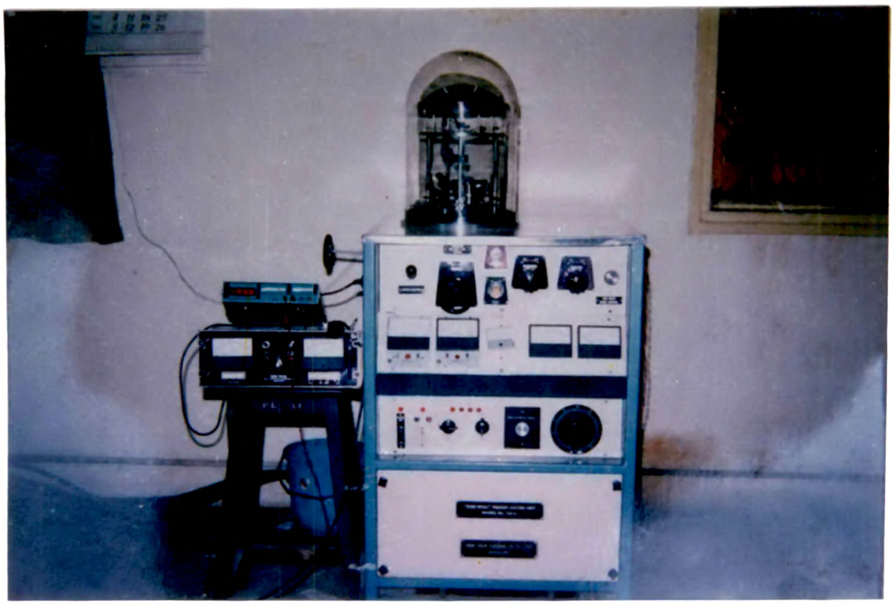


Fig.4

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

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 the 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 D P. is connected with a water-cooled baffle valve which enables a working vapour pump to be isolated while pumping system is at atmospheric pressure. A liquid nitrogen trap is also connected with the D.P 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 connections 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, 50mA 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 stabilised 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 5Pa to 10^{-2} Pa and a Penning gauge fitted with the chamber and measuring from 10^{-1} Pa to 10^{-5} Pa.

3.2 Chamber arrangement :

The chamber gadgetary comprises of a work holder ring which has a useful diameter of about 8 inches. It is supported by three pillars fitted to the base plate. A D.C. high tension discharge cleaning system consisting of a pure aluminium annular ring suitably shielded to avoid electron contamination of the work. A source shutter swinging over the source position and operated by an external lever is provided on the front of the cabinet.

A standard filament holder is fitted to the L.T.live electrodes and an earth electrode. The filament is normally positioned vertically below the centre of the work holder to give nearly uniform distribution of the vapours. For deposition of a multilayer film, it is provided with a multifilament turret designed to evaporate four different materials without breaking the vacuum. The turret is rotated by external hand wheel.

Rotary Drive : The rotary drive is useful for uniform deposition of materials on large plane surface substrates. This consists of a work holder of 6 inches in diameter and is rotated by a variable speed electric motor situated outside the chamber. The speed is controlled by a solid state speed control.

III. THICKNESS MEASUREMENT :

Thickness is the most significant film parameter. It may be measured either by in-situ monitoring or after the film is taken out of the deposition chamber. Usually for in-situ thickness measurement a quartz crystal monitor is used. It can be used for monitoring and controlling the rates of deposition of both metals and non-metals. The monitor utilizes the 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 reasonance frequency irrespective of the thickness, density, elastic constant or stiffness of the added material.

The thickness of deposited film is obtained by the formula[5]

$$t = \frac{df}{C_f r^{(\mathrm{film})}} \qquad (3)$$

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 cleaning of the crystal in case lower activity or failure of oscillation of the crystal, by dissolving Al in NaOH.

V. OPTICAL MICROSCOPY :

VICKERS MICROSCOPE :

The microphotographical study of the crystal surface was carried out using the Vickers projection microscope (Figure-5). It is an inverted metallurgical type optical microscope. For examinaton of the crystals, this microscope carries two different system. The present work involve optically opaque crystals and only the reflection system was used for the purpose. This equipment also provides for phase contrast and light profile techniques.

VI. X-RAY DIFFRACTION ANALYSIS :

Among the various characterization techniques, X-Ray diffractometer techniques play a very important role in structural characterization. These techniques are used for a microstructural investigation of thin films and bulk crystals. The techniques based on the use of monochromatic radiation yield quantitive structural and symmetry properties possessed by the material being

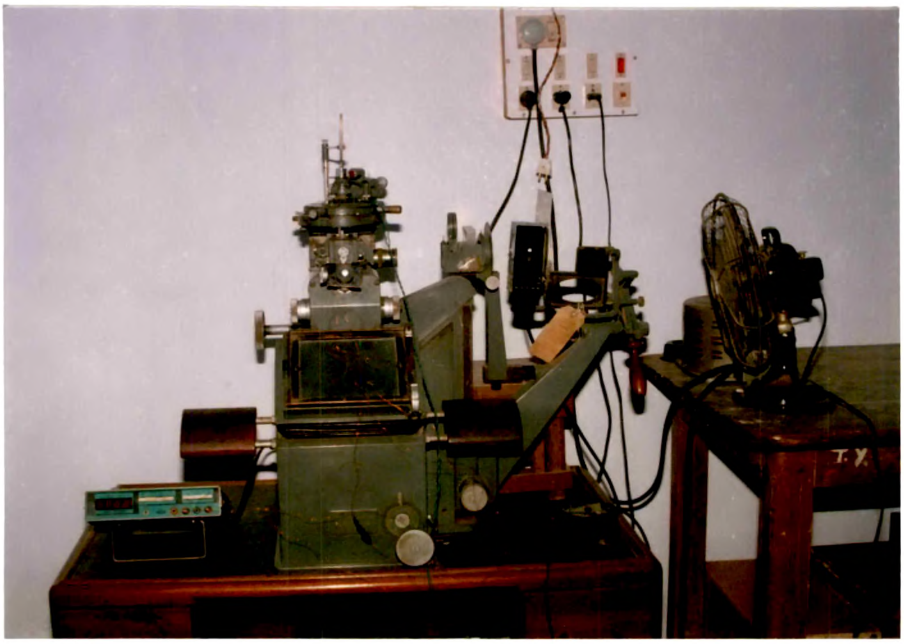


Fig.5

investigated. In the present study the X-ray diffractometer, Philips PM 8203 with pw 1390 channel control and pw 1373 goniometer have been used for the characterization of $In_{0.1}Bi_{1.9}Te_3$, $In_{0.2}Bi_{1.8}Te_3$ and $In_{0.5}Bi_{1.5}Te_3$ crystals. It was operated at 35 to 40 kV and 20 mA with Cu target ($\lambda = 1.5418Å$).

VII. MICROHARDNESS MEASUREMENT TECHNIQUE :

The Vickers Microhardness Tester (supplied by M/s. Cooke Toughton and Simms ltd. England) was used with the Vickers projection microscope[6] (Figure-5). All the instructions suggested by the supplier were rigidly observed. Since there is no provision for making indentations at high temperature in the above equipment a special arrangement described below was attached to the hardness testing apparatus.

A cylindrical shape refractory block (Figure-6) was used to mount the specimen, the diameter and length of this block being such that it can easily be fitted in the collect of hardness testing unit of the microscope. A small heating element was passed through this mount. A circular brass disc of the same diameter as of the mount was fitted on top of this mount. The specimen can be fitted on the disc by a proper adhesive. A copper constantan thermocouple was placed through a groove 1mm below the top of the brass disc. Known melting points of some substances like paraffin wax, InBi, Tin etc., were checked to

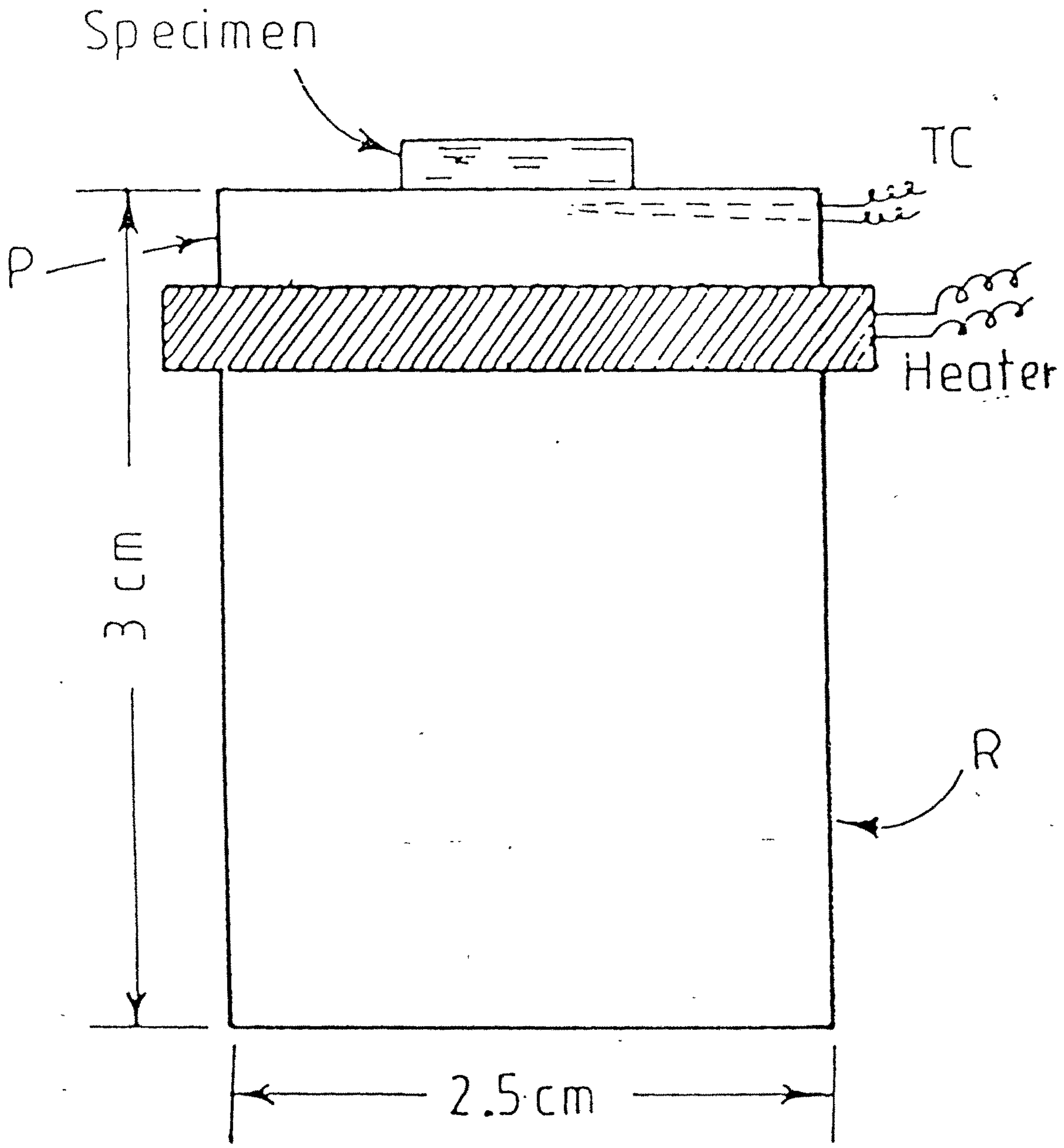


Fig.6

calibrate this heating arrangement. The error in any case did not exceed 2°C. Before indenting the specimen, care was taken to get the thermal equlibrium. The detailed study of hardness of $In_xBi_{2-x}Te_3$ with (x = .1 to 0.5) crystals at room temperature and at higher temperatures is presented in Chapter-7.

VIII. ELECTRICAL PROPERTIES :

The discovery of a great number of semiconductors among the intermetallic compounds has created an urgent need of methods to make fast accurate mesurements of resistivity. Various sample geometries of films are in use; such as clove geometry and linear four probe geometry as described by Van der Pauw[7] and Goswami[8]. For high value of resistance, linear four probe geometry in advisable. A sensitive current-meter and a stable power supply are connected in series with the sample. The voltage measurement is made by a sensitive and preferably a digital voltmeter. For resistivity measurement on crystals, the Valde's four probe geometry is used. Here, the pointed tips of closely spaced probes are contacted on the sample surface. The method does not required the probes to be ohmic[9]. This set-up is shown in Figure-7.

For Hall measurement, linear four probe geometry is used. Charge carriers contributing the current caused by an applied electric field are deflected by a magnetic field applied perpendicular to the current. The resulting Hall voltage

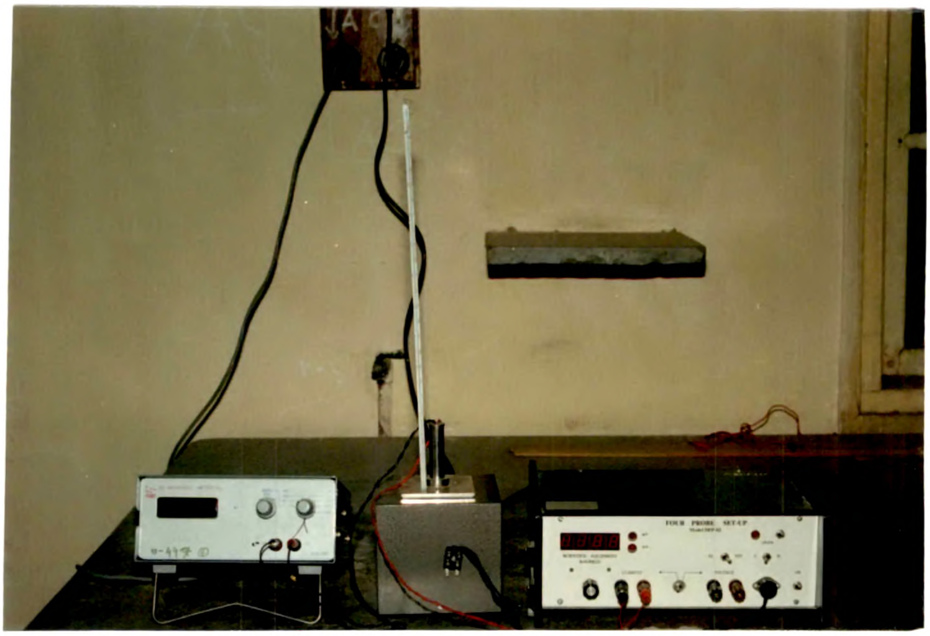


Fig.7

normal both to the current and the field can be measured. The sample is kept between the two poles of a strong electromagnet (Figure – 8) capable of magnetic field of the order of 18 kilo gauss. A sensitive current meter is connected in series with a stabilished DC power supply and a sample. Across the other two contacts, digital microvoltmeter is connected. Current and voltage are measured in absence and presence of the magnetic field. For both the measurments, the electrodes should be ohmic.

Thermoelectric power measurements :

For the measurement of Seebeck coefficient [thermoelectric powere (TEP)] as a function of temperature, a "Differential Temperature controller" developed by Scientific Solutions, Bombay, was used (Figure-9). The thermopower measurement system TPSS-200 (Figure-9) is a versatile, low cost, specially developed integrated system for measurement of the thermo e.m.f. generated by the "Sample – stainless steel probe couple" in presence of a temperature gradient. The two matched main heaters mounted along the axis of the two sample holder shafts provide the controlled base temperature from 300 to 500 K. The auxiliary heaters wound on each of the sample holder shafts enable to provide the required gradient upto ± 10 K. The sign of the gradient can be changed by altering the choice of the auxiliary heaters.

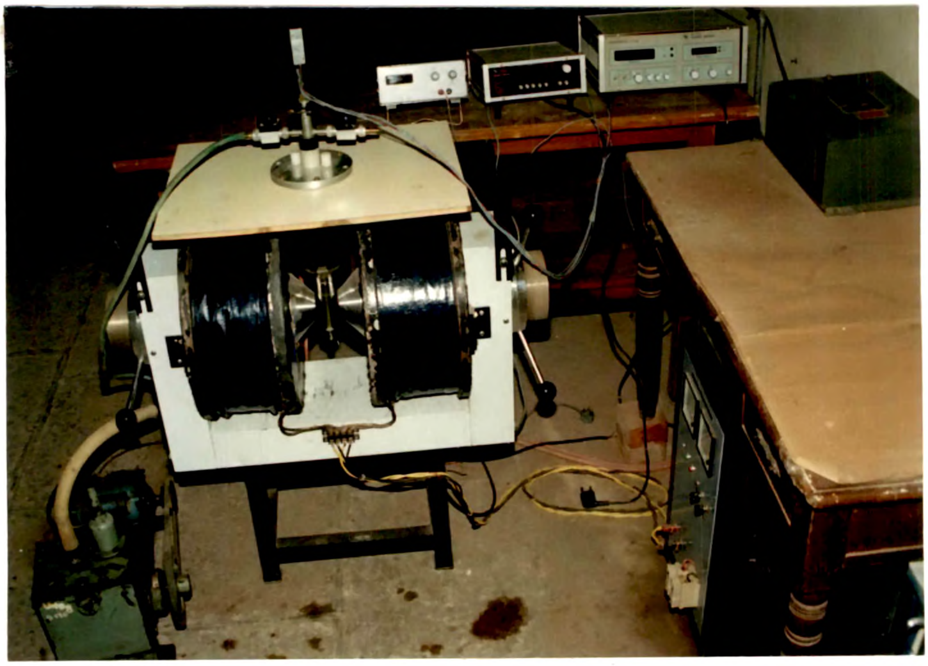
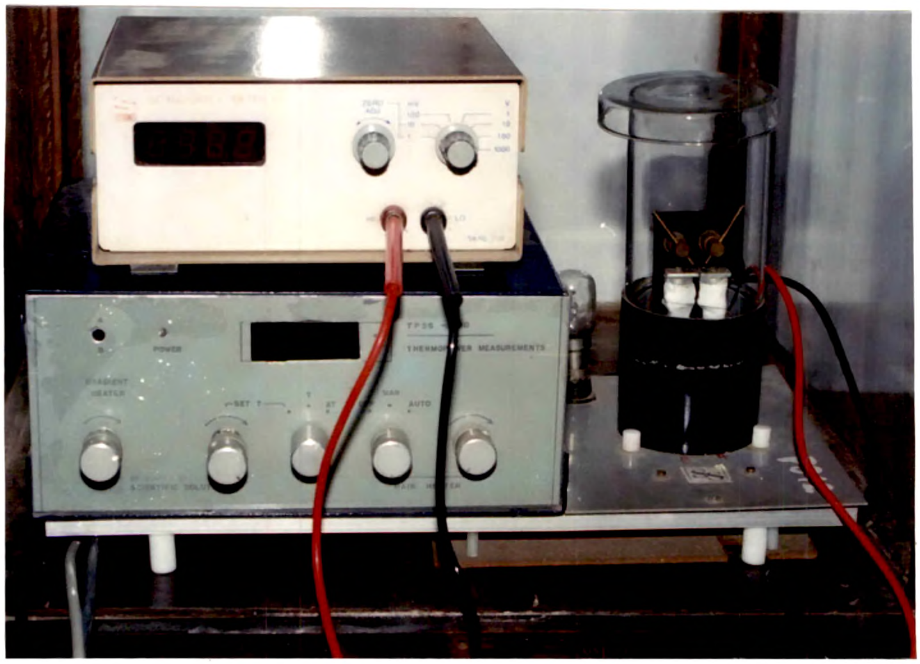


Fig.8


ZERO ADJ
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GRADIENT HEATER
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MEASUREMENTS
MAIN HEATER

Fig.9

IX MEASUREMENT OF OPTICAL PROPERTIES :

The I.R.Spectrophotometer (BOMEM. Canada, MB100 Figure – 10) was used for measurement of optical absorption or transmittance of the samples, in the wave number range 510cm^{-1} to 4000 cm^{-1}. In the case of crystals, fine crystalline powder was throughly mixed with spectroscopic grade dry KBr powder at about less than 5% concentration and the mixture was formed into a palette of about 1cm, diameter using a vacuum palettizer. Whereas, in the case of thin films, the films deposited on KBr crystal substrates were used. The resolution of the instrument in 4cm^{-1}. It uses glowbar IR source and DTGS detector[10].

Fig.10

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