CHAPTER – 5

EXPERIMENTAL TECHNIQUES

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 Choromel-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.

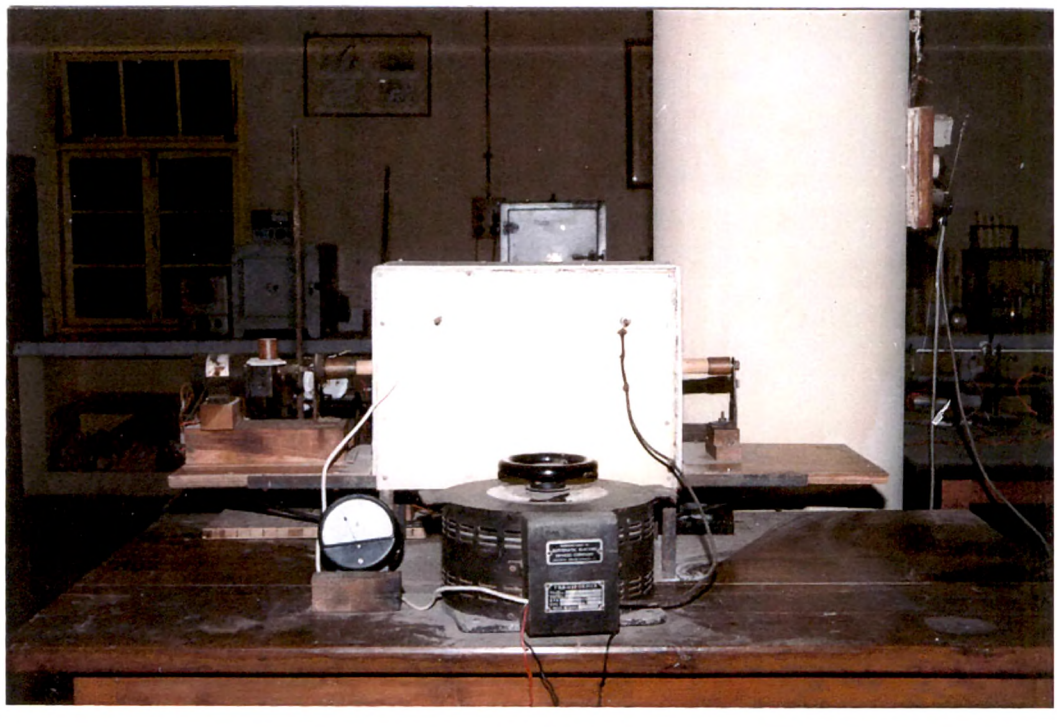

Figure -1

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

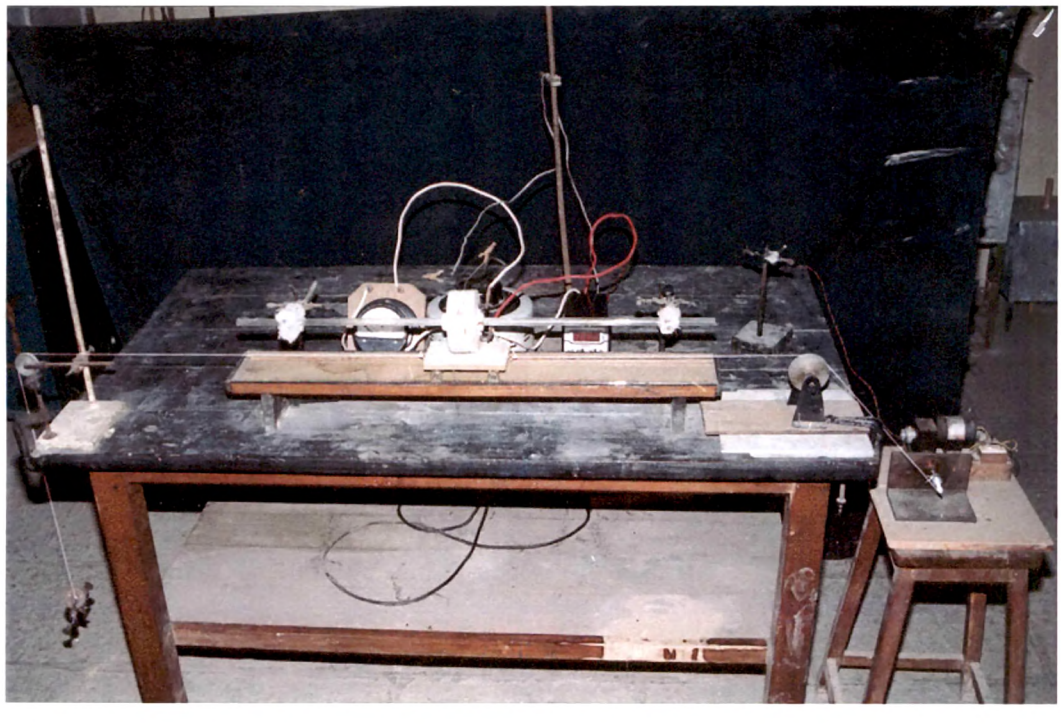

Figure -2

shown in Figure - 2. The vacuum sealed quartz tube containing the charge was then kept inside the long quartz tube. At a maximum temperature of 600 ^{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 $Bi_{1-x}Sb_x$ 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 each pits. The etch pit count method is used to estimate dislocation density.

OPTICAL MICROSCOPY:

Vickers microscopy and hardness testing:

The micro topographical 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

Figure -3

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.

The Vickers micro hardness 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. 3). 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.

The Vickers hardness H_v, was calculated using the formula,

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

in accordance with the definition given by Cooke, Toughton et al[3],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.

ELECRICAL PROPERTIES:

The discovery of a great number of semiconductors among the intermetallic compounds has created an urgent need of methods to make fast accurate measurement 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 [4] and Goswami [5]. For high value of resistance, linear four probe geometry is 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. Change of resistivity with temperature is studied by keeping the sample in vacuum of the order of 10^{-4} Pa in order to prevent oxidation. For heating the substrate, radiant heater is used. The temperature is sensed by a

thermocouple which is kept in similar conditions with the substrate. Externally, the thermocouple is connected to a digital millvoltmeter to measure the thermo –EMF. For resistivity measurement on crystal, 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 require the probes to be ohmic[4]. This set up is shown in figure-4

For Hall measurement, linear four probe geometry is used. Charge carrier contributing the current caused by an applied electric field are deflected by a magnetic field applied perpendicular to the current. The resulting Hall voltage normal both to the current and the field can be measured. The sample is kept between the two poles of a strong electromagnet capable of magnetic field of the order of 18 kilo gauss. A sensitive current meter is connected in series with a stabilized DC power supply and the 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 measurements, the electrodes should be ohmic. The Hall measurement set up is shown in Figure-5.

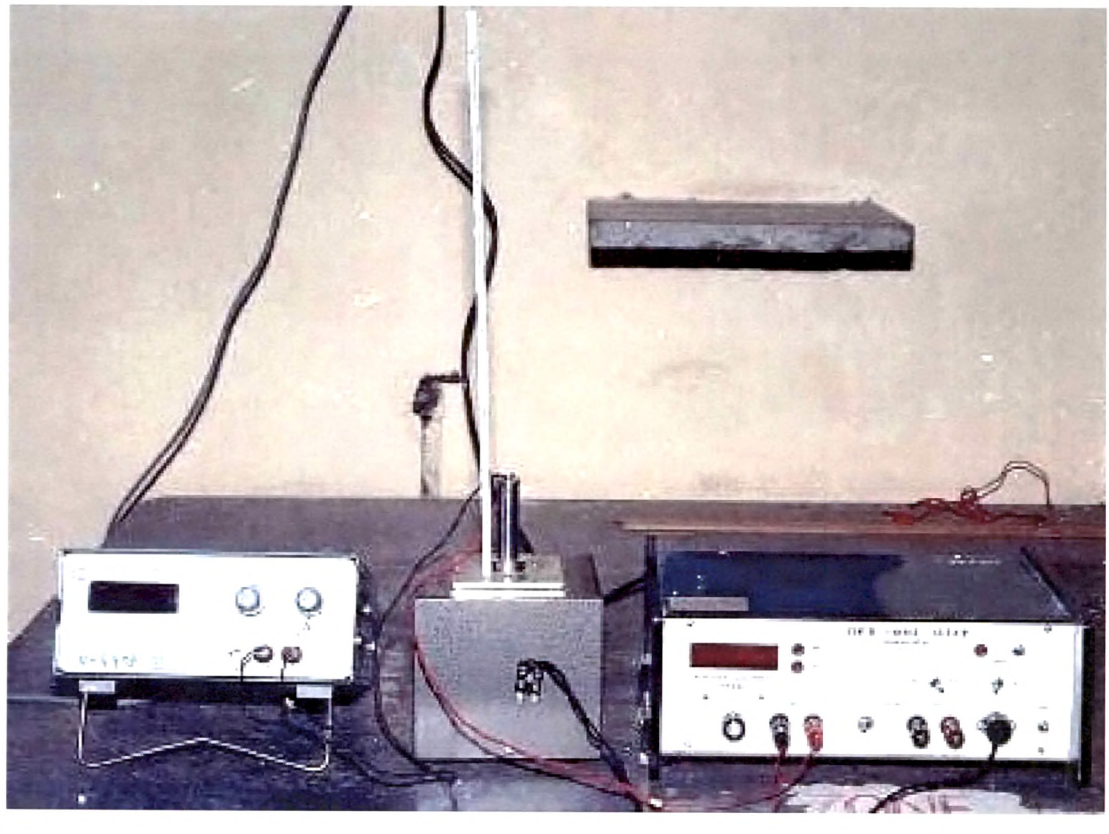

Figure-4

Figure-5

Thermoelectric power measurement:

For the measurement of Seeback coefficient as a function of temperature, a "Differential Temperature controller' [Scientific solution, Bombay] was used. The thermo power measurement system is shown in figure 6. The set up [model : TPSS-200] is a versatile, low cost, specially developed integrated system for measurement of the thermo E.M.F generated. 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 heater wound on each of the sample holder shaft enables to provide the required gradient upto 10 K. The sign of the gradient can be changed by appropriate selection of the auxiliary heater coils.

The operation of the system can be understood from figure -7 which is based on the principle of AC power control using controlled rectifiers. Using triacs as the power control device the power to the heater and hence the temperature can be controlled. An error signal proportional to the difference of the measurement and the set temperature along with external bias is used to decide the firing angle of the triac hence controlling the temperature.

The out put of the sensor mounted on the main heater is amplified by the preamplifier U1 to get the voltage proportional to the temperature reading which is displayed as T. The same signal is also fed to the error amplifier U2

which compares this signal with the set temperature signal obtained from a stable reference source. The gain of the error amplifier controls the proportional band of the control and is presetted to about 30 % of the full scale.

The error amplifier output is then summed with a bias signal from the bias control in the summing amplifier U3, the out put of which is the voltage proportional to the temperature different. Preamplifier U5 amplifies the out put of the differential thermocouple for the indication of ΔT.

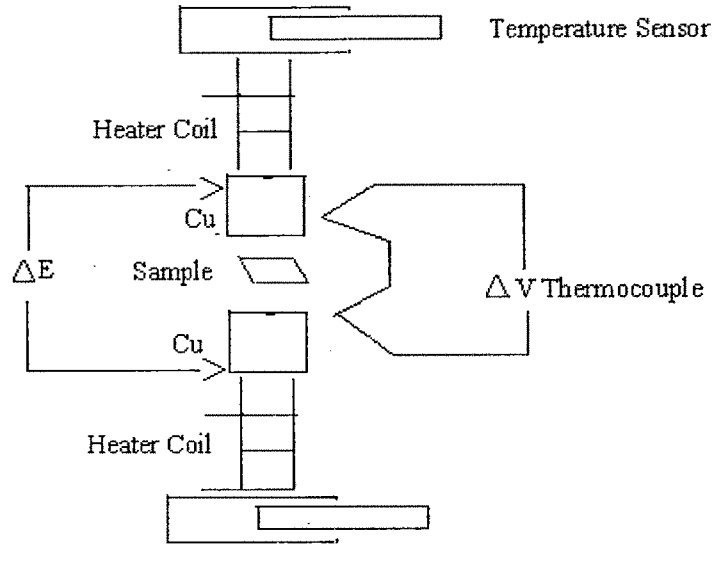

Figure-6 Block diagram of sample holder of TEP set up

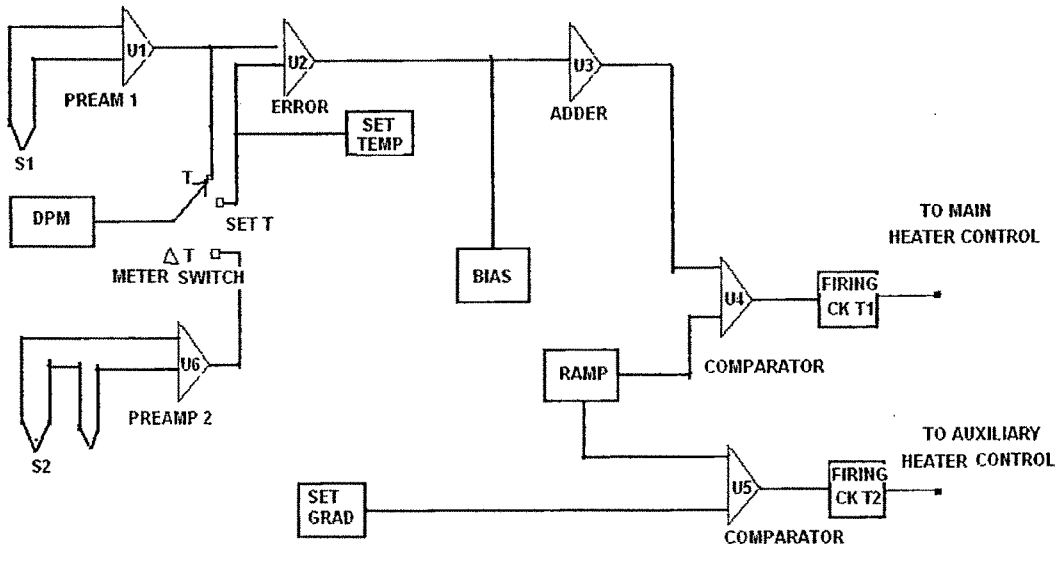

Figure-7

THIN FILM PREPARATION TECHNIQUE:

Vacuum Coating System: In the present work, for the thin film deposition "Hind Hivac" vacuum coating unit, Model No 12 A – 4 Figure – 8 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 desiccant 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 desiccant which absorbs the water vapour present in the gas. This avoids contamination of the rotary pump oil with water and other harmful vapours.

Figure-8

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 gadgetry comprises of work holder ring, which has a useful diameter of 8". A D.C. high tension discharge cleaning system consists of pure aluminum 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[7].

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

where df is the frequency shift, C_f is a constant, characteristic of the crystal and ρ 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.

In the present work the thin films of $Bi_{1-x}Sb_x$, of different thicknesses were deposited on glass substrates at 10^{-4} Pa pressure. The thickness of these films was measured by quartz crystal monitor.

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 "beam splitter", 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 beam splitter. 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 wavelength range 1500nm to 20,000nm was measured using IR spectrometer [BOMEM, Canada, MB 100 Figure-9]. The films to be measured were deposited on KBr crystal substrates. 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[8,9].

Figure-9

Table – 1

Spectrophotometer 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}

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