CHAPTER 2

EXPERIMENTAL TECHNIQUES

There are several techniques utilized 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[1,9] and Zone Melting [2,9] crystal growth methods, X- ray diffraction, preparation of thin films and measurement techniques of optical and surface observation etc.

I. TECHNIQUES FOR CRYSTAL GROWTH

1.1 VACUUM SEALING UNIT:

The stoichiometric amounts Bi-Sb-Te of the materials were weighed accurately up to 10 micrograms using a semi microbalance (Fig.1) and filled in a quartz ampoule of about 8 cm in length and 1cm in diameter. The quartz tube was then vacuum sealed at a pressure of about 10^{-5}Pa (Fig.2).

Fig.1 Weighing Machine **Fig.2 Vacuum Sealing Unit**

1.2 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-3. A quartz ampoule evacuated to about 10^{-5} 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 ± 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.

Fig. 3 ALLOY MIXING UNIT

1.3 Crystal growth:

Crystal growth is complex process, which usually takes place by a phase change, and it can broadly be categorized 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 susceptible to modifications. Also chances of chemical contamination are reduced compared to other methods. All the basic techniques are variants in the way materials can be crystallized in rods, crucibles, boats or tubes. Thus the Czochraslki technique involves controlled crystallization from a crucible by pulling the melt whereas the Kyropoulos technique does not involve pulling but crystallization on to 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 transverse 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-Stockbargermethod:

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 (+5℃) using a chromel-alumel thermocouple and a temperature controller. The temperature gradient in the furnace in the region of interest. Viz the lower end where through the molten charge is lowered for unidirectional solidification. Could be varied in the range from about 35^0C/cm to 45^0C/cm. The ampoule containing the charge is sealed are 10^{-5} 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 facilitatedby a gear mechanism couple with a 0.5 H.P motor. The lowering speed could varied from 0.35cm/hr to 1.0 cm/hr by changing the output shaft of the gears. A photograph of the unit is shown in Figure-4.

Fig.4 BRIDGMAN-STOCK BERGER TECHNIQUE

(2) ZONE MELTING TECHNIQUE:

Growing single crystals by the zone melting method is one of best technique (fig.5). In this method the ingot is placed in a long quartz tube. The size of ingot was about 6 cm in length and 0.8 to 1 cm in diameter. In this method a small molten zone is created in a large solid ingot of the material to be crystallized and passed from one end of the ingot to the other. As the zone travels, it redistributes impurities along the charge after the 10 passes and finally we got self-nucleated Single crystal. By giving a necessary sufficient time to the first molten zone we got good quality of Single crystal. Growth velocity is an important factor in this technique. The growth velocity was 1 cm / hr. Crystals with x up to 0.3 were grown at the same growth velocity and temperature gradient. The temperature gradient across the two solid – liquid interfaces was obtained to be about 65 ^{0}C / cm by controlling the furnace temperature within $\pm$ 1 ^{0}C, giving a zone length of about 1-2cm. To obtain good quality crystals, it was found necessary to give sufficient time to the first molten zone before starting the zone travel to achieve stable conditions. The quality of the crystals obtained was judged by examining the cleavage surfaces and obtaining dislocation density.

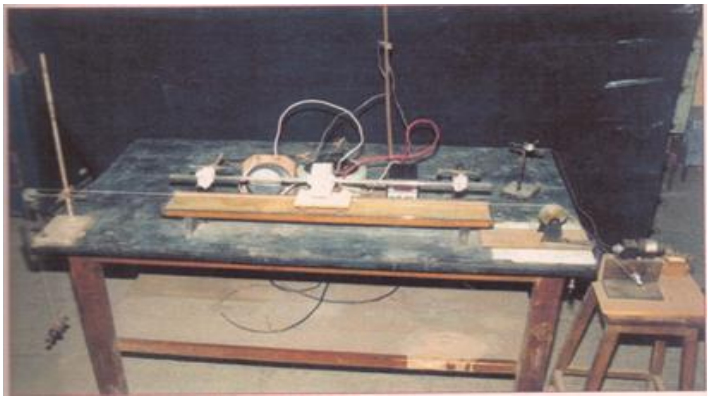

Fig.5 ZONE MELTING UNIT

1.4 X-Ray diffraction techniques

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 substances this fact is basis for the use of diffraction method for chemical analysis. X-ray powder diffraction (XRPD) techniques are used to characterize samples in the form of loose powders or aggregates of finely divided material .qualitative analysis for a particular 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 routinely differentiate between phases having the same chemical composition but different crystal (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 in to 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 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 angel 2θ many modern automated powder diffractometers can provide further data reduction ,including peak finding a tabular listing of peak an intensity versus interplanar spacing employing ,search/ match software and other computer utilitiesPhase identification using XRPD is based on the unique pattern produced by every crystalline phases. 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, all of these methods make use of the database maintained by the JCPDS international center of diffraction DATA [10].

1.5 Energy dispersive analysis by X-rays (EDAX)

The technique EDAX is based on the simple concept of production of x-rays by elements. A beam of electrons about 0.5 μm in diameter is made to strike the specimen surface under investigation. The electron beam interacts with the atoms in the specimen to produce x-rays, which are characteristic of the specific atoms. The x-rays are analyzed according to their energies. The generated x-rays are made to enter a liquid Nitrogen cooled Si diode detector doped with Li which intercepts the x-rays. The intercepted x-rays generate photoelectrons which eventually dissipate their energy by creating electron-hole pairs in the diode (which is reverse biased). These created electron-hole pairs are separated by the junction to develop a voltage pulse signal. This voltage signal is proportional to the energy of the incident- rays and the number of pulses per second is a measure of the incident intensity of x-rays of that particular energy. Thus, the measurement of it after suitable amplification gives information about the energy of the x-rays incident. Thus, characteristic x-rays emitted by different species of atoms in the specimen can be identified by the measurement of number of voltage pulses and their magnitudes as functions of x-ray energy. As the Si diode detectors have a resolution of about 150 eV, the minimum energy that can be detected without overlap of the peaks is about 150 eV. This energy dispersive analysis of x-rays is less sensitive than the EPMA or WDAX by a factor of about 20. The EDAX is usually available with the Scanning Electron Microscope (SEM) where the electron beam falling on the specimen can also generate characteristic x-rays which can be analyzed by EDAX using a silicon diode detector.

Fig. 6 Scanning Electron Microscope and EDAX System Setup

1.6 PELLETIZER UNIT:

In this unit we make crystal pallet for characterization studies at the pressure level up to 30 mbar with KBr. For this purpose it has also provide a set of Dai. This unit is working on the oil pressure system. (Fig. 7)

Fig. 7 PALLETIZER UNIT

1.7 FTIR TECHNIQUE:

The I.R. Spectrophotometer (FTIR, Japan,Jasco, 4100)[8] was used for measurement of optical absorption or transmittance of the samples, in the wave number range 400 cm^{-1} to 4000 cm^{-1}. In the case of thin films, the films deposited on NaCl crystal substrate were used. The instrument acquires an interferogram and transforms it into a spectrum in terms of wave number. The wave number resolution of the instrument is 4 cm^{-1} . It uses glowbar IR source and DTGS detector.

The theoretical and experimental investigations of the optical behavior of solids deal primarily with optical reflection, transmission and absorption properties, and their relation to the optical constants both of the bulk and thin film forms. As a result of these studies, complex multilayer optical device systems with remarkable reflection, antireflection, interference and polarization properties have emerged for both laboratory and industrial applications. The absorption studies have led to a variety of interesting thin film optical phenomena which have thrown considerable light on the electronic structure of solids.

The optical measurement constitutes the most important means of determining the band structure of semiconductors. For absorption studies, photons of selective transmission/absorption are used. Optical properties of a thin film generally differ from those of the bulk. The differences are usually attributed to the microstructure of the films.

Principally there are several methods to determine the optical constants, such as Abbe’s method, spectroscopic methods, polarimetric method and critical angle method. The spectroscopic method is probably the most widely used one for optical measurements. The most direct and the simplest method for determining the band structure is to measure the absorption spectrum.

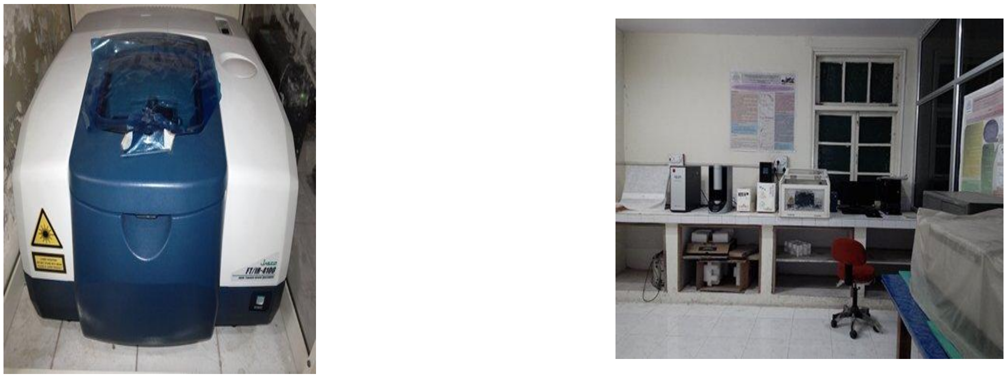

Fig.8 FTIR TECHNIQUE

1.8 MICRO HARDNESS MEASUREMENT TECHNIQUE

Vickers Microscope:

The micro photographical 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. The present work 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.

Measurement techniques:

Hardness can be measured by various methods:

1. Scratch method

2. Abrasive method
3. Plowing method
4. Rebound method
5. Damping method
6. Cutting method
7. Erosion method and
8. Static indentation method

A brief description of these methods follows:

1. **SCRATCH METHOD:**

   In 1822, Friedrich Mohs developed this method which is widely used by mineralogists. In this method, ability of one material to scratch another is termed as the hardness of scratched – material with respect to the other. If the hardness is greater than 4, Mohs method is not suitable.

2. **ABRASIVE METHOD:**

In this method, measure of resistance to mechanical wear is taken to be the amount of material from the surface under specific conditions. Here the specimen is loaded against a rotating disc and the rate of wear is taken as the hardness measure.

3. **PLOWING METHOD:**

Here a blunt element (usually diamond) is moved across a surface under controlled conditions of load and geometry. The width of the groove produce is taken as the measure of hardness. The Bierbaum test is of this type.

4. **REBOUND METHOD:**

In this method usually a steel ball of standard mass and dimensions is bounced from the test surface and the height of rebound is taken as the measure of hardness. The Shore scleroscope is a hardness tester of this type.

5. **DAMPING METHOD:**

Herein, change in amplitude of a pendulum having pivot resting on the test surface is the measure of hardness.

6. **CUTTING METHOD:**

A sharp tool of specific geometry is made to remove a chip of standard dimension from the specimens.

7. **EROSION METHOD:**

In this method, abrasive grains or sand is caused to impinge on the test surface under standard conditions and loss of material in a given time is taken as the measure of hardness.

8. **STATIC INDENTATION METHOD:**

In this method, a steel ball, a pyramid or a cone (indenter) is forced into the surface and the load per unit area of the permanent impression formed is taken as measuring of hardness. The Brinell, Vickers, Rockwell, pin indentation and knop tests are of this type.

The most popular and simplest method of hardness measurements is the static indentations hardness method.

- **VICKERS DIAMOND INDENTER:**

The Vickers diamond indenter is in the form of square based pyramid with semi apex angle = 68°. It was used to measure the microhardness of the grown single crystals by producing indentation marks on the cleaved surfaces of the specimens, under known applied loads, loading time, temperature etc. Its main characteristic is the geometrically similar impressions obtained. The Vickers hardness, $H_{v,}$ was calculated using the formula,

$$H_v = \frac{1854 \times P}{d^2} \text{kg/mm}^2 = \frac{1854 \times P}{d^2} \times \frac{9.8 \text{ MPa}}{1} \qquad (1)$$

in accordance with the definition given by Cooke, Toughton et al [5], 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 eye piece with the least count 0.19 micron was used.

The Vickers Microhardness Tester (supplied by M/s. Cooke Toughton and Simms Ltd., England)[6] was used with the Vickers projection microscope (fig. 9). 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 (fig.10) 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 proper adhesive. A copper constantan thermocouple was placed through a groove 1mm below the top of the brass dics. Known melting points of some substances like paraffin was, InBi, Tin etc., were checked to calibrate this heating arrangement. The error in any case did not exceed 2ºC. Before indenting the specimen, care was taken to get the thermal equilibrium. The detailed study of hardness of $Bi_{2-X}Sb_XTe_3$ (X = 0, 0.05, 0.1, 0.2) crystals at room temperature is presented in chapter 4.

Fig.9 HARDNESS MEASURING INSTRUMENT

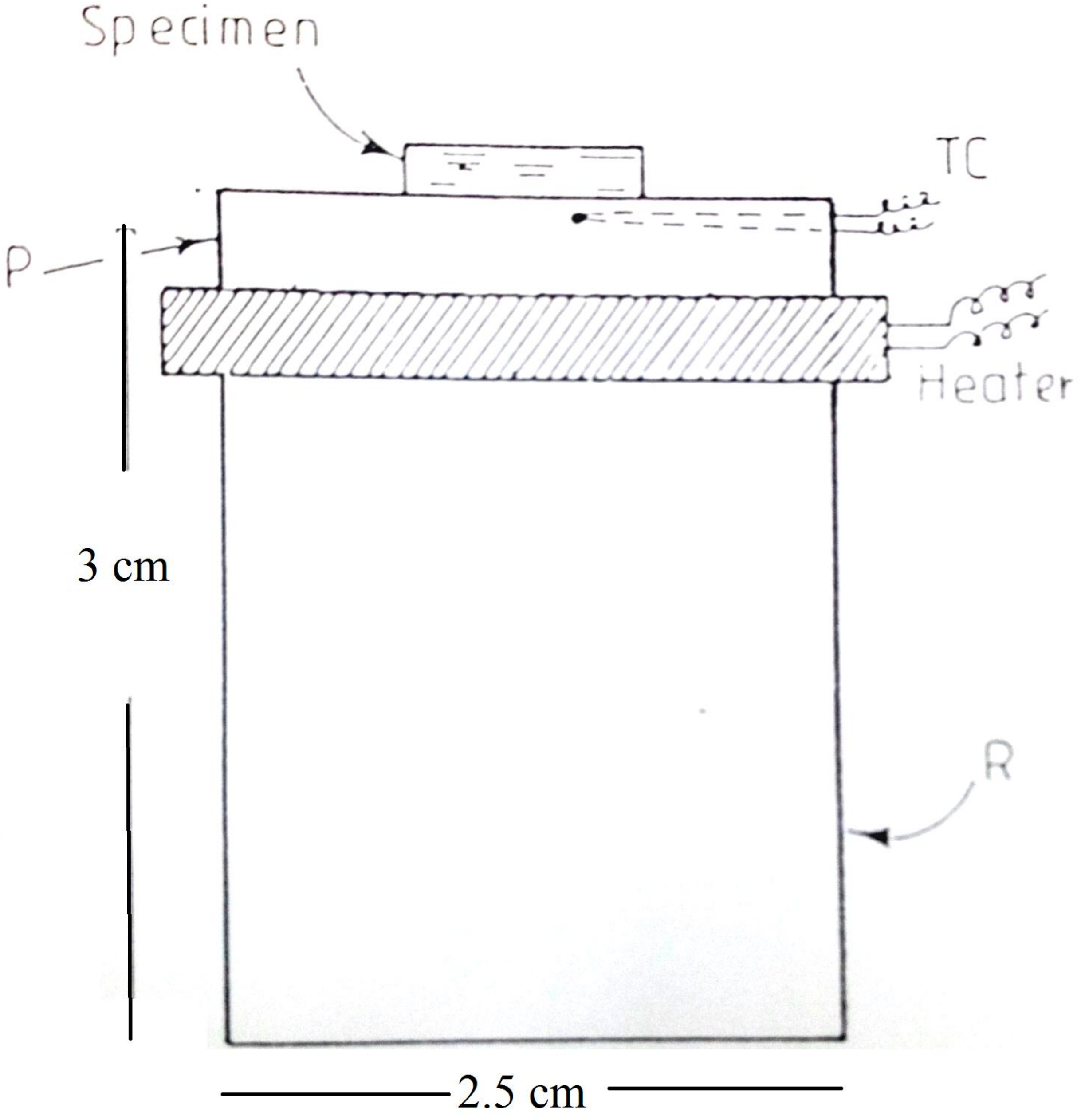

Fig. 10 High Temperature Hardness Test Sample Holder

1.9 THIN FILM UNIT:

Modern day technology requires several types of thin film for a variety of applications. 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:

(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 tehniques such as reactive evaporation sputtering and plasma deposition have also been developed. The PVD technique has been used in this investigation.

PVD techniques are fartherclassified 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[5]. 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 pressures $\leq 10^{-4}$ pa, the mean free path of molecules becomes large so that the vapour beam reaches the substrate nearly unscatered.

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 difficulties 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, In order to overcome these difficulties, the technique 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 case, vapours impinging on the substrate are highly supersaturated so that the film composition is not affected by condensation coefficients. In this technique, a fine powder of the compound is sprinkled over a heated sheet boat, which is at a high temperature 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 temperature 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 10KV and focused 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 3000^0 C. At such a high temperature, most of the refractory metals and compounds can be evaporated. The temperature at the focused 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 usually 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 the 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 on 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 accelerates the ions to a desire energy[4].

Thickness Measurement Techniques

While the various techniques commonly used for thickness measurement: among the quartz crystal monitor has been used for thickness measurement.

a) Quartz Crystal Monitor/Digital Thickness Monitor:

The digital thickness monitor which is used by the author allows direct display of film thickness and rate of deposition during the evaporation. An oscillator quartz crystal with frequency of 6 MHz is positioned in the vacuum chamber so that vapour is deposited both on the substrate and defined area of the crystal. A second crystal (reference) having frequency of 6.4 MHz is positioned inside the monitor. The difference of 400 Hz initially is mixed with the output from a variable frequency oscillator to produce zero reading before each deposition. When deposition takes place on the crystal, a difference in the crystal frequency oscillator to produce zero reading before each deposition. When deposition takes place on the crystal, a difference in the crystal frequency is created which is amplified and fed into a circuit where it is converted to a D.C. Signal and the thickness of film is displayed on the monitor.

In the present work the thermal evaporation technique has been used to grow thin films of $B_{i2-x}Sb_xTe_3$(x=0, 0.5, 0.1)

Vacuum coating system:

HINDHIVAC has developed an advanced coating system (Box Type High Vacuum Coating Unit Model BC-300, BC 600)[7] (Fig. 11) that meets all the requirements for modern thin film technology, which is capable of producing clean ultimate vacuum up to 10 m.bar. These Box Coater units are specially developed to meet the growing demands of the optical/semiconductor coating and other electronic device manufacturers and it is designed taking into consideration of all the aspects of the overall performance for producing repeatable and also reproducible products.

Fig. 11 THIN FILM COATING UNIT

The pumping system is designed for faster pump down time of the chamber with cleanest possible vacuum conditions. The whole chamber gadgetry is designed to produce components with excellent uniformity fitted with optional rotary/planetary drives, ion bombardment facility, and LT evaporation facility. 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.

The Box Coater has wide range of applications: Cold light mirrors Laser mirrors Protective hard glass layers on plastics Reflection & Anti-reflection layers Anti-corrosive layers Semi-conductor layers, Electrically conductive & Transparent layers, Protective coating against solar radiation Interference Filters, Contact layers.

The basic Box Coater unit consists of high vacuum chamber gadgetries such as rotary drive, ion cleaning system etc. and vacuum pumping system consisting of rotary vacuum pump, fore line trap, Right angle isolation valve, and air admittance valve etc., Microprocessor based digital pirani gauge & penning gauge. Box Coater System can be offered with diffusion pump or imported Turbo/cryopump. The cubical vacuum chamber in this Box Coater is made out of stainless steel and the inner walls polished to achieve low degassing rates to reach better ultimate vacuum. The base plate is provided with number of ports.

It has also Optional Accessories3 KW Electron Beam Gun 270 bent beam with single source/4-source, 3 KW power supply. Digital Thickness Monitor or 8 KW 270 bent beam with single source/4-source, 3KW power supply.

References:

1. Bridgman, P.W., Proc. Am. Acad. Arts: Science, 60 (1925) 303.
2. Pfann, W.G., Trans. AIME, 194 (1952) 747.
3. Ueda R. and Mullin J. B.: Crystal growth and Characterization north-Holland publishing company, New York (1975).
4. Chopra K. L. and Malhotra K. L.,: Thin film technology and applications, Tata McGraw-hill publishing Co. Ltd., New Delhi, (1985).
5. Goswami A., Thin Film Fundamentals, New age international publishers, London, 42(1996).
6. Cooke Toughton and Simms, Photomicrography, NY (England), 146(1996).
7. Instruction Manual, Vacuum Coating Unit, BC-300, Hind High Vacuum Co. (P) Ltd., Bangalore.
8. Instruction Manual, FT/IR 4100, JASCO, Japan.
9. Dhanaraj, G.; Byrappa, K.; Prasad, V.; Dudley, Springer Handbook of Crystal Growth, XXXVIII (2010)1818p.
10. Joint Committee on Powder Diffraction Standards (JCPDS), International Centre for Diffraction Data, Swarthmore, PA.