PART - B
CHAPTER - V

EXPERIMENTAL TECHNIQUES
A general discussion of the experimental techniques used in this field of studies is presented in this chapter. It includes the techniques of synthesizing the alloys, compounds and their crystal growth and dissolution, preparation of thin films and measurement techniques of optical and electrical properties, surface observation etc..

SYNTHESIZING THE COMPOUND:

For synthesizing the compound a simple but efficient stirring method has been used. A quartz tube is passed through a horizontal furnace 60cm in length, which gives a uniform temperature zone of about 15cm, and is rotated at one r.p.m. by a motor attached to one of its ends [Fig. 1]. The vacuum sealed (2X10^-5 Torr) quartz ampoule containing the starting materials with appropriate weight proportion is inserted in this quartz tube. The temperature is kept about 100°C above the melting point of the compound. The rotation of the quartz tube gives rocking movement to the ampoule and stirs the molten charge. Usually, one-day rotation followed by the idle run of one-day is found sufficient. After this the molten charge is slowly cooled or quenched as desired. In the present case, since SnSe, SnS, SnTe and SnSe₂ are equilibrium compound phases, slow cooling was
employed. To avoid oxidation due to possible breaking of the ampoule while cooling, the ampoule containing charge was inserted in another tube which is also sealed under vacuum ($2 \times 10^{-5}$ Torr). This method enables one to prepare fairly homogeneous compounds.

**CRYSTAL GROWTH:**

For crystal growth of such binary intermetallics, the Bridgman-Stockbarger and Zone-melting techniques are suitable. Present author has used the former one. The furnace made for this purpose consists of two halves with two independent power supplies [Fig.2] for the upper and lower sections. Their temperatures can be varied independently and hence the gradient between the two could be varied. The proportional temperature controllers controlled the two furnace temperatures accurately to within $\pm 5 ^\circ$C. The lowering of the ampoule was effected by a motor with a gear mechanism to reduce the speed. The lowering speed could be varied from 0.4 to 1.5 cm/hr. by changing the gear system.

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

1. Cleavage test
2. Etching test
3. X-ray technique

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

OPTICAL MICROSCOPY:

VICKERS MICROSCOPE:

The microtopographical study of the crystal surfaces 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 being the transmission and the other reflection system. The present work in this thesis involves the 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 TECHNIQUE:

Laue back reflection photographs of the single crystals were taken using Philips no. 1009 type X-ray generator and Laue camera supplied with it. The unit was operated at 35KV and 20 mA using tungsten target. A distance of 3cm was kept between the film and sample. The sample was mounted in such a way that the X-ray beam was normal to the cleavage plane of the crystal.
The Laue diffraction technique is the simplest of X-ray techniques. It usually yields qualitative information and requires a specimen in the form of a single crystal. The radiation used is normally white X-ray from Tungsten target. In the standard technique there are two modes: Back reflection pattern and transmission pattern. Most frequently a well defined crystal plane of a sufficiently thin crystal is held perpendicular to the incident X-ray beam and with a sufficient time of exposure, the Laue photograph is obtained, either in the back reflection zone or in the transmission zone. The most significant applications include determination of crystal orientation, symmetry and qualitative perfection. The pattern is characteristic of the particular orientation of the crystal. Additionally if crystal symmetry axis coincides with the incident X-ray beam or a symmetry plane is parallel to the incident beam, the resulting pattern shows corresponding symmetries. This feature of the pattern can be fruitfully used to confirm indices of the crystal plane normal to the incident beam. The sharpness of the Laue spots is a measure of crystal perfection. The technique in general can prove very versatile with suitable modifications\(^{(1)}\). In the present work the Phillips No. 1009 X-ray generator and the goniometer and Laue camera supplied with it were used.
MICROHARDNESS TEST:

The Vickers micro hardness was measured using Vickers diamond indentor [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°. 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 jig.

A cylindrical shape refractory block 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 through 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°C. Before indenting the specimen, care was taken to get the thermal equilibrium.

The Vickers hardness Hv is defined as the ratio of applied load to the
pyramidal contact area of indentation and turns out to be \( (2) \)

\[
H_v = \frac{1854 \times P}{d^2} \text{ Kg/mm}^2
\]  

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 least count 0.125 micron was used.

**KNOOP HARDNESS TEST:**

The Knoop microhardness tests were carried out using Knoop indenter supplied with the C-Z Vertical microscope. The indenter is in the form of a rhomb based pyramid with semi-apex angles 130° and 172° 30'. There is no provision for making indentations at high temperatures with this microscope. A chief characteristic of this indenter is that, it is sensitive to anisotropy along the indented surface. The Knoop hardness is calculated with the formula \((3)\):

\[
H_k = \frac{41230 \times P}{d^2} \text{ Kg/mm}^2
\]  

where \( P \) = applied load in grams, \( d \) = length of major diagonal of the indentation mark, in microns. To measure the diagonal of the indentation mark, a micrometer eye-piece with least count 0.816 micron was used.

**THIN FILM PREPARATION:**

In the present work, thin films were deposited using “HIND HIVAC” vacuum coating unit, Model No.12 A-4 [Fig-4]. The chamber
Fig. 4
material is polished stainless steel with vacuum sealed quartz 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 capacity of 200 Lit/min and an oil diffusion pump OD-114 having oil charge of 150cc to 200cc. Rotary pump is connected with a moisture trap mounted directly above the inlet of the pump. A trap containing the dessicant in the form of pellets [activated Alumina granules] 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 pump oil being sucked back.

To avoid the back streaming and hence contamination and loss of pump fluid, the diffusion pump is connected with 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 diffusion pump to avoid the back streaming and increase the action of diffusion pump.

An L.T. supply to excite filament or boat and an H.T. supply for
glow discharge cleaning (ion bombardment), are provided in the system.

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 0.5 Torr to $10^{-3}$ Torr and the Penning gauge fitted with the chamber measures from $10^{-2}$ Torr to $10^{-6}$ Torr.

**CHAMBER ARRANGEMENT:**

The chamber gadgetory 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 L.T. live electrode and earth electrode. The filament is normally positioned vertically below the centre 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 / filament. A stainless steel wire mesh is fitted over the base plate to prevent foreign bodies falling into the baffle valve.

**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 upto
a temperature 250°C to 275°C in about 30 minutes. Temperature measurement is made 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 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 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

$$t = \frac{df}{C_r r (\text{film})}$$

where df is the frequency shift, $C_r$ 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.
OPTICAL MEASUREMENT:

A dual beam spectrometer [Shimadzu, Japan, UV 365, Fig. 5] was used for measurement of optical absorption, transmittance and reflectance of the samples, in the wavelength range 2500 nm to 190 nm. From 2500 nm to 808 nm, it uses PbS detector and changes to photomultiplier detector for wavelengths from 808 nm to 190 nm. For illumination in the range 2500 nm to 303 nm, tungsten halogen lamp is used and below 303 nm a deuterium lamp is used. It is also provided with two monochromators (prism and grating) for better filtering. The average resolution available is 0.5 nm. For measuring optical properties of single crystals, cleavage slices with thickness about 0.03 cm to 0.85 cm were used. These samples were pasted on a thick black paper with a cut exposing the crystals to the incident light. The reference used was a replica of the black paper, having the cut of the same size and in exactly the same position. This arrangement was necessary because the crystal size was smaller than that of the sample compartment. For reflectance measurement, standard aluminium coated mirror was used as reference. In the case of thin films, films coated on glass substrates were used against identical blank glass substrates as references.

The absorbance in the range 15,000 nm to 20,000 nm was measured using IR spectrometer [BOMEM, Canada, MB 100, Fig. (6)]. The films to be measured were deposited on KBr crystal substrates and were mounted on
the sample holder. The instrument acquires an interferogram and transforms 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\(^{(G)}\).
REFERENCES:


