CHAPTER 4

Measuring Equipments, Sample Preparation and Experimental Technique

4. Introduction

In this chapter, details of the preparation of Bi$_2$S$_3$ thin-films, Bi$_2$O$_3$ thin-films, Al/(p)Bi$_2$S$_3$ Schottky junction, Sn/(p)Bi$_2$S$_3$ Schottky junction and (p)Bi$_2$S$_3$-(n)Bi$_2$O$_3$ heterojunction have been discussed. The experimental procedures for measuring structural, electrical, optical etc. properties on these samples have been discussed. Brief descriptions of experimental setups required in the present investigations have presented.

4.1 Material used for sample preparation

Bi$_2$S$_3$ and Bi$_2$O$_3$ were used to prepare all thin film samples and junctions for the present investigations. The specifications of these two materials are given in Table 1.

Table 4.01; Samples and their specifications:

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Group</th>
<th>Form</th>
<th>Company</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_2$S$_3$</td>
<td>V-VI</td>
<td>Powder</td>
<td>Sigma Aldrich Co. U. S.A.</td>
<td>99.00%</td>
</tr>
<tr>
<td>Bi$_2$O$_3$</td>
<td>V-VI</td>
<td>Powder</td>
<td>Sigma Aldrich Co. U. S.A.</td>
<td>99.999%</td>
</tr>
</tbody>
</table>
4.2 The evaporating system and its operation

The vacuum coating unit (Vico model VC-12; M/s Vacuum Instruments Co. New Delhi) was used to deposit all films (samples and electrodes) in the present investigation (Photograph 1). The experimental setup for depositing thin films is shown in Fig.16. The coating chamber consists of a 30cm diameter bell jar made of corning glass and a base plate having 12 numbers of holes to be used for connecting different elements such as thermocouple, power supply to electrodes, substrate heater etc. through insulating material. Single phase rotary pump (model-Vico, VC-12) fitted with magnetic air admittance cum isolation valve and four stage diffusion pumps (model A-105SS) are used to create high vacuum (about $10^{-5}$ Torr). A heater of 500W is attached with the diffusion pump to heat up diffusion pump oil. A water circulation system is used to cool the diffusion pump. For getting high vacuum, high quality silicon oil have been used in the diffusion pump.

To note the fore pressure of the chamber during roughing the chamber as well as during baking the diffusion pump a pirani gauges is fitted with the coating unit. For measuring the low pressure inside the chamber a gauge head of a penning gauge was fitted to the base plate.

For any deposition (sample, electrodes) by coating unit, properly cleaned vacuum chamber is very much essential so that the chamber becomes free from any kind of contamination. In the first step of deposition, the chamber was cleaned by using isopropyl alchohol. For uploading substrates along with mask, substrates holder having slits of desired shapes have been used. The sample sources to be deposited, substrates with suitable shape of mask, a heater for maintaining substrate temperature and a
thermocouple to note substrate temperature were loaded inside the properly cleaned chamber.

In the present case for deposition of electrodes and barrier metals by thermal evaporation, filament source heater in the form of helical coils was used. The source heater was clamped at the two ends of two copper plates, which in turn were fixed at the top of the lead in electrodes inside the chamber by steel screws. The helical coils were of tungsten wires of 0.5mm diameter and of 10 cm length with at least 5 to 7 turns.

For holding masks and substrates a circular aluminium plate was specially designed consisting of slits of desired sizes on which mask could be placed and the substrate could be placed on the masks. The mask holder was supported by three metallic rods within the bell-jar, the distance of the masks from the source heater could be adjusted. The arrangement for thermal evaporation inside the vacuum chamber is shown in Fig.17.

For depositing a sample the vacuum chamber is cleaned properly. The arrangement for thermal evaporation (for samples or electrodes) was made as shown in Fig.17. Then pressure of the vacuum unit was lowered up to about 10^{-2}\text{Torr} by operating Rotary pump only, the backing valve and the roughing valve was opened and closed alternately to create vacuum in upper and lower chamber of the vacuum unit and pressure of the chambers was measured by by pirani gauges fitted with the coating unit. When the pressure of the vacuum chamber reaches about 10^{-2}\text{Torr} the heater switch of the diffusion pump was on to heat up the diffusion pump oil. Cold water was circulated around the diffusion pump to control the temperature of the diffusion pump. When the diffusion pump oil was heated to sufficiently high temperature, diffusion pump was allowed to function by opening baffle valve and the pressure of the chamber was noted.
by penning gauge fitted to the base plate. Within few minutes the pressure of the chamber decreases up to about $10^{-5}$ Torr. At this stage the samples to be deposited were heated to evaporate by manipulating currents of source heaters from outside. During films deposition, the temperature of the substrate heater was controlled from outside and observed with the help of thermocouple. The sample vapour reaches the substrates and condensate onto the substrates, thus thin films were formed. After completion of deposition the baffle valve was closed and switch of diffusion pump heater, substrate heater, source electrode were off. The rotary pump and the water circulation were allowed to continue till the temperature of the diffusion pump was decreased to nearly room temperature (about 306K).
Fig. 16: The schematic view of evaporating system. A-Bell jar, B- Neoprene rubber gasket Substrate heater,  C- Base plate, R-Shutter, D-Fillament, G- Penning gauge F-Pirani gauge, N-Air admittance valve, H-Baffle valve, J-Water cooling pipe, I-Diffusion pump, I- water cooling coils K- Diffusion pump heater, G-Roughing valve, L-Backing valve, O-Magnetic air admittance valve, P-Rotary pump.
4.3 Substrate preparation

Glass is most widely used as substrate material for depositing polycrystalline films. In the present study microscopic glass slides of thickness 1.35mm (Upen Instruments, Nashik, India) were used as substrate material to deposit all types of films by thermal evaporation technique.

The substrates were cleaned using the following procedures to eliminate any possible sticking particles and impurities from them.

(i) The microscopic glass slides were cut in different sizes and washed with ordinary detergent solution.

(ii) This washed glass slides were treated by a boiling mixture of nitric acid and isopropyl alcohol in a beaker.
(iii) Finally, the slides were put into another container and washed with freshly prepared distilled water and then immersed in isopropyl alcohol and afterwards these were again rinsed with de-ionised water.

The cleaned slides were put vertically in a cleaned petry dish separated from one another and allowed to dry. Necessary precaution was taken in drying and preserving the substrates till its use, so that it remains free from any air born contaminations. These were heated inside a cleaned closed stainless steel oven for one hour at 373K before use.

4.4 Mask generation

For various types of measurement (optical, electrical, structural, thickness etc.), samples of different sizes and shapes were required. These were obtained by masking substrates during deposition to get the desired area deposition of the substrate during deposition. In the present case, the masks were prepared by cutting good quality mica sheets with sharp edge blades. Mask of various patterns used in the present deposition are shown in Fig.18. The masks were thoroughly cleaned by detergent and finally washed in acetone. They were dried properly by hot air blower before placing in the vacuum chamber.
4.5 Preparation of semiconductor films

The Bi$_2$S$_3$ films required to study optical, electrical and surface morphology were prepared by evaporating Bi$_2$S$_3$ powder from tantalum boat source. The sample specification is given in Table 4.01. It has been observed that Bi$_2$S$_3$ powder decomposes [1, 2] during vacuum evaporation and sulphur evaporates faster than bismuth affecting the stoichiometry of the deposited films. During direct evaporation of Bi$_2$S$_3$, sulphur reaches the substrate first and forms sulphur film then bismuth is deposited over the sulphur film. If deposition is continued the Bi film over the sulphur film becomes thicker and thicker. Which creates problem in the process of Bi$_2$S$_3$ film formation, In order to overcome these problems, the remaining residue of the source (Bi$_2$S$_3$) was removed after a certain interval of time and deposition was re-started with new Bi$_2$S$_3$.
powder, this process was continued till the suitable film thickness was achieved. The
distance between sources to substrates was maintained approximately at 7cm. As-
deposited films were annealed in air inside an oven at 473K for 3 hours. During films
deposition substrate temperature was maintained at room temperature (303K). The
schematic presentation of different types of thin films prepared in the present
investigation has been shown in Fig.19.

Fig.19: Thin films of (p)Bi$_2$S$_3$ for; (a) optical properties, (b) electrical properties,
(c) Hall effect measurement, (d) SEM measurement.
The thin films of $\text{Bi}_2\text{O}_3$ of various shapes and sizes required for electrical, optical, structural etc. studies were vacuum deposited onto the chemically cleaned glass substrates from platinum boat source. The specification of the samples is given in Table 4.01. During deposition, pressure of the chamber was kept at about $10^{-5}$ Torr and substrate temperature was maintained more or less at room temperature (303K). Distance between substrates and source was made approximately at 7cm. It has been observed that $\text{Bi}_2\text{O}_3$ powder decomposes during evaporation [3, 4]. So, all as-deposited films were annealed in air inside an oven at 443K for 3 hours. Fig.20 shows schematic presentation of some $\text{Bi}_2\text{O}_3$ films.

Fig.20: Thin film of (n)$\text{Bi}_2\text{O}_3$ for; (a) optical properties, (b) electrical properties, (c) Hall effect measurement, (d) SEM.
Fig. 21 (i) Schematic diagram of Al/(p)Bi$_2$S$_3$ Schottky barrier junction.

Fig. 21 (ii) Schematic diagram of Sn/(p)Bi$_2$S$_3$ Schottky junction.

Fig. 21 (iii) Schematic diagram of cross-sectional view of Al/Bi$_2$S$_3$-Ni Schottky junction.
4.6.2 Preparation of (p)Bi$_2$S$_3$/(n)Bi$_2$O$_3$ heterojunctions

Three parallel strips of Nickel each of width 0.1 cm and length of 1.8 cm were thermally deposited onto a freshly cleaned glass substrates from an electrically heated tungsten spiral, above these electrodes, (p)Bi$_2$S$_3$ films of area 1.5×1.3 cm$^2$ were thermally deposited by following the same procedure as mentioned in section (4.7). The composite sample was annealed in vacuum at 465K for 3 hours. The (n)Bi$_2$O$_3$ films were deposited over the annealed (p)Bi$_2$S$_3$ films by using the same procedure as mentioned in section (4.7). The composite sample was again annealed in vacuum at 465K for 3 hours. Over these composite films, three Al electrodes of width 0.1 cm and length 1.8 cm were vacuum deposited. Thus nine heterojunctions of same area over a single substrate were formed. The schematic presentation of the Ni-(p)Bi$_2$S$_3$/(n)Bi$_2$O$_3$-Al is given in Fig. 22(i) and crosssectional view of the junction is presented in Fig. 22(ii).

During preparation of Ni-(p)Bi$_2$S$_3$/(n)Bi$_2$O$_3$-Al junctions two samples with Al/(p)Bi$_2$S$_3$= Ni and Ni/(n)Bi$_2$O$_3$-Al were also prepared for each set. The work work function of Bi$_2$O$_3$ is 6.23eV [5]. The Ni (work function 5.13eV) was found to form Schottky contact with (n)Bi$_2$O$_3$. In this case the condition given in section (3.6.2) of Chapter 3 was not followed, which might be due to high surface state over the (n)Bi$_2$O$_3$ thin film surface as discussed in section (3.6.2). The doping concentration of respective films was measured from reverse biased $C-V$ characteristics using relation (3.43) of Chapter 3.
Fig. 22 (i) Schematic diagram of (ii) (p)Bi$_2$S$_3$/n)Bi$_2$O$_3$ heterojunction.

Fig. 22 (ii) Schematic diagram of Crosssectional view of Ni-(p)Bi$_2$S$_3$/n)Bi$_2$O$_3$-Al Structure.
4.7 Doping

Doping was done on the films to make the films n-type or p-type. The Bi$_2$S$_3$ films were doped with In (Indium metal) by simultaneous co-evaporating Bi$_2$S$_3$ powder and a very small amount of In (percentage wise) from two sources simultaneously. The doped Bi$_2$S$_3$ films were annealed at 473K for three hours. The Bi$_2$O$_3$ films were doped with Sn (Tin) by co-evaporating Bi$_2$O$_3$ powder and a very small amount of Sn metal (percentage wise) simultaneously. The Sn doped Bi$_2$O$_3$ were annealed at 443K for three hours. The In doped Bi$_2$S$_3$ thin films were found to be p-type and Sn doped Bi$_2$O$_3$ thin films showed n-type nature when tested by hot probe technique. Both (p)Bi$_2$S$_3$ and (n)Bi$_2$O$_3$ thin films are highly resistive and determination of type of doping and doping concentration of both type of films was not possible by Hall Effect measurement [6]. So, the type of the semiconducting films was determined by hot probe method.
4.7.1 Determination of the type of doping

A simple experimental setup developed in our laboratory for determining the type of a semiconducting film by hot probe method is shown in Fig.23. In this process one terminal was connected to the sample through a mini heater and another terminal was directly connected to the sample. The hot probe developed positive thermo-emf in the millivoltmeter indicating n-type nature of the semiconducting film. The reverse signified the p-type nature of the film.

4.8 Thickness measurement

For thickness measurement, number of films of different sizes and shape were deposited in one set. The setup for measuring thickness is shown in photograph 2. A substrate whose half portion was coated along with the samples [Fig.24(a)] was selected from the set for measuring thickness applying interferometric method developed by Tolansky [7]. The thickness of the sample was considered to be the thickness of the whole set. A layer either of silver or aluminium was vacuum deposited over the half portion of the sample extending up to sample free region as shown in the Fig.24 (b). The Al or Ag film makes a step at the edge of the sample film. A semi transparent film was prepared by depositing silver onto a glass slide Fig.24(c). The silver coated film and the half silvered film was housed in thickness measuring setup as shown in Fig. 25(a)
The thickness measuring setup consists of monochromatic sodium light, focusing lenses, half silvered glass, beam splitter and a telescope. The semi-transparent glass slide was placed so that a wedge shaped air film was produced between the sample film and the semi transparent glass. The light reflected back by sample film with the step and semi-transparent film produced interference fringe along with fringe shift in the field of view of the telescope. The interferometric fringes observed are shown in Fig.25(b). Thickness of the film was measured by measuring fringe width and fringe shift. For a sample film if \( d \) is the width of the fringe and \( D \) is the shift of the fringe, the thickness of the film \( t \) is given by

\[
t = \frac{D\lambda}{d} \tag{1}
\]

where \( \lambda \) is wavelength of the monochromatic radiation used.
4.9 Measurement of optical properties

For the measurement of optical transmittance, absorbance and reflectance of Bi$_2$S$_3$ and Bi$_2$O$_3$ thin films, a UV-Visible spectrometer CARRY 300 (Varian, Victoria-3170, Australia) was used (photograph 3). This is a computer based instrument. The detail of the spectrometer is in the literature [1]. The experimental arrangement of the spectrometer is shown in Fig.26. The Cary-300 has been equipped with an Integrating Sphere (model DRA-CA-301) for measuring transmittance, absorbance and reflectance of the films. The schematic view of the integrating sphere with accessories is shown in Fig.27.
4.9.1 Integrating Sphere and its Working Principle

Radiation from the main source is converted into monochromatic wave by grating and the range of wavelength is from 200nm to 900nm. This monochromatic radiation of the instrument is split into two different beams; the sample beam and the reference beam. Each beam is interrupted alternately and periodically by means of a chopper such that the integrating sphere is illuminated alternately by the two beams through two different windows (one beam passes through the sample and another beam directly to the integrating sphere). In this way samples are scanned from 200nm to 900nm to get spectra. At any given wavelength, the instruments record the ratio of the signal produced by the detector when the sphere is illuminated by the sample beam to that when the sample is illuminated by the reference beam. The sphere efficiency factor for a given sample is a function of many variables including the spatial distribution of the energy reflected from the sphere, the reflectance of the sphere wall, the geometry of the sphere (location of ports and baffles etc.) and the efficiency of the detector itself. The detector is a PMT 928 having range 200nm-900nm.

The integrating sphere measures reflectance and transmittance factors, commonly called reflectance and transmittance. The relative spectral reflected (transmitted) is defined as the ratio of the flux reflected (transmitted) by the specimen to that of a standard surface under identical geometrical and spectral conditions. For transmittance the standard surface is air and for reflectance the standard surface is a secondary white standard calibrated relative to the perfectly reflecting diffuser.
Because of the geometry of the integrating sphere, it has the ability to collect most reflected or transmitted radiation, remove any directional preferences and present an integrated signal to the detector.

Fig. 26: Optical arrangement of the spectrometer (Cary-300).
4.10 Microstructural, morphological and compositional analysis

4.10.1 X-ray diffraction studies of the samples

Philips X-ray diffractometer (Philips X’Pert Pro) with CuKα radiation of wavelength 1.54056 Å was used to take X-ray diffraction spectra (photograph 4). The diffractometer operated at 40KeV and 30mA. X-ray diffrectogram analysis including the peak search was done by computer programming Phylips X’pert software. The detail of analysis is given in section (5.1.1) and (5.1.2) of Chapter 5.

Fig.27: Top view of the integrating sphere (DRA-CA-301) and accessories.
4.10.2 Scanning of Electron Microscope (SEM) studies of the samples

Scanning electron micrograph (SEM) of the films were taken with the help of a Scanning Electron Microscope (LEO 1430VP) with an operational voltage 15KV (IIT, Guwahati) (photograph 6). The detail analysis is given in section (5.2) of Chapter 5.

4.10.3 Compositional analysis by XRF and by Energy Dispersive X-ray Analysis (EDAX)

Quantitative compositional analysis was done by X-ray Fluorescence (XRF) spectra and recorded by XRF spectrometer (AXIOS PANlalytical) at the Sophisticated Analytical Instrument Facility (SAIF) of Gauhati University (photograph 5). The detail analysis is given in section (5.3.1) of Chapter 5.

Quantitative compositional analysis was done by Energy Dispersive X-ray Analysis (EDAX) by FET Quanta 250 SEM, at Monipur University. The detail analysis is given in section (5.3.2) of Chapter 5.

4.11 Arrangement for measuring $I-V$ characteristic, photoconductivity and photovoltaic effect

To study the electrical properties on both (p)Bi$_2$S$_3$ and (n)Bi$_2$O$_3$ thin films and their Schottky barrier and heterojunctions, various types of samples were prepared as shown in the Fig.19, Fig.20, Fig. 21 and Fig. 22. The preparation details have been presented in the previous section. The experimental arrangement for taking $I-V$ characteristics of the samples (gap type, Schottky barrier junction and heterojunctions) in dark and under illumination is shown in Fig.28. The experimental setup is shown in
photograph 7. It consisted of two coaxial metallic cylinders. The inner cylinder was supported by the outer cylinder and the annular space was used to put the sample for study. The outer cylinder was provided with a side tube fitted with an air tight glass window. The window was fitted with a shutter such that the annular space can be made completely dark by closing the shutter. The upper end of both cylinders were joined together and made airtight by “O” ring and screw arrangement. The bottom of the inner cylinder remains free and the bottom of the outer cylinder was connected to a rotary pump, used to evacuate the annular space during experiment. A specially designed and fabricated sample holder (Fig.29) was vertically clamped to the outer surface of the inner cylinder so that the sample when mounted on it faced the glass window. The insulating frame of the sample holder was fixed by screws to provide necessary electrical connections. Four conducting strips were fixed on the insulating frame to make pressure contact with the electrodes. Shielded wires from the sample holder, thermocouple wire and temperature sensor were brought out of the chamber through air tight fitted at the top of the assembly.
Fig. 28: Experimental setup for measuring $I$-$V$ characteristic under vacuum, in air, in dark, under illumination at different light intensities and at different temperatures. $L_1$, $L_2$- lens arrangement, $A$- cylinder, $A'$- inner cylinder, $G$- glass window, $S$- shutter, $F$- arrangement for filter, $E_1$- electrodes, $H$- heater, $T$- temperature controller, $D$- diffusion pump, $P$- rotary pump.

Fig. 29: The sample holder for electrical measurements.
Fig. 30: Chamber for housing light source.

Fig. 31: Spectral irradiance curve of 6315-1000W QTH Lamp.
Light source

Special light source was designed and fabricated to study the samples under illuminated condition, the Quartz Tungsten Halogen (QTH) lamp (500w) was mounted on a ceramic base housed in rectangular wooden box fitted with a cooling fan (Fig.30). The power of the QTH could be adjusted varying the input voltage of the lamp from 0 to 12V. The lamp gave high visible and near infrared output with little ultraviolet. The infrared part of the radiation was filtered out by using a water filter. It had a smooth spectral curve and a stable output in the wavelength range 250 nm to 2500 nm (Fig.31). The ray of light was made parallel using lens and allowed to fall on the sample through a glass window. The intensity of the light was measured by a LUX meter (LUSOMET 300 ED).

The QTH lamp was used to measure sample properties under white light. For this purpose intense light from QTH source was connected at the focus of a planoconvex lens where IR part of the ray was filtered out by using a cool water filter. The parallel ray from it were allowed to fall on the sample through the glass window with the help of a shutter.

To study the spectral response a monochromator (Model77200, Oriel Instruments, USA) was used and QTH was used as the light source for the monochromator. The monochromatic light of the monochromator was allowed to fall on the sample through the glass window of the specially designed vacuum chamber Fig. 28.
4.11.1 Study of electrical properties of a gap type thin film sample

The experimental arrangement for measuring $I-V$ of gap type samples at different temperatures is shown in Fig.32. The sample was mounted on the sample holder and the shutter of the glass window was closed to make the annular space of the cylinders totally dark. To measure the temperature of the sample, a thermocouple (chromel-alumel) was loaded such that the tip of the thermocouple touches the film and the thermo e.m.f. of the thermocouple was observed through a digital microvolt meter (Agronic-112) connected to the thermocouple. During experiment the pressure was lowered up to about $10^{-3}$Torr by operating rotary pump connected to the system. A constant voltage source was connected in series.

The current passing through the sample was recorded from a picoammeter connected in the circuit. The potential drop in the sample was recorded by a microvoltmeter connected in parallel with the sample. The sample was kept at various temperatures using a electronic temperature controller and corresponding current passing through the sample and voltage drop in the sample was recorded.
The pressure of the vacuum chamber was lowered up to about $10^{-2}$ Torr by operating rotary pump. Then the sample was studied for $I-V$ characteristic under different environmental conditions.

**4.11.2 Recording of $I-V$ curves of Al/(p)Bi$_2$S$_3$; Sn/(p)Bi$_2$S$_3$ and Ni/(n)Bi$_2$O$_3$ junctions**

A specially designed sample holder shown in Fig.29 was used to load the junction sample. The sample with the sample on it was housed inside the vacuum chamber as shown in Fig.29. The experimental arrangement and electrical connections to the samples to study the $I-V$ characteristics of Schottky barrier junction and heterojunction under dark and illuminated condition is shown in Fig.33. An X-Y/t recorder (M/s Didital Electronics Ltd. Bombay, Model; Omnigraphic 2000) was used for this purpose. The bias voltage source was either a variable ramp (Systonics, Model 1014) or a source meter (Scientific Electronics ps-25). The voltage of the junction was recorded along the X-axis and the current was obtained by recording voltage drop across a standard resistance along Y-axis of the recorder. In some cases instead X-Y/t recorder, a...
microvoltmeter (Agronic-112) and a current meter (Keithley, UAS, Model 6514) was used. The voltage of the junction was directly measured by microvolt meter and current flowing trough the junction was directly measured by current meter.

Fig.33: Arrangement of X-Y/t recorder for measurement of $I-V$ characteristics.

4.11.3 Capacitance-voltage measurement

To study $C-V$ characteristics of a junction, the junction was housed inside the chamber along with sample holder. The sample was properly connected to Auto Compute L-C-R Q meter (APLAB-4910), and capacitance was measured under reverse biased condition Fig.34. A variable DC power supply (Scientific Electronics model: PS 25) was used for applying bias voltage.
Fig. 34: Arrangement for capacitance-voltage measurement.
Photograph 7: Instrumental arrangement for measuring $I-V$ characteristics in dark, under illumination, at different temperatures and photovoltaic effect.
References


