CHAPTER - III
3.1 Sample Preparation:

The preparation of glasses takes place normally by continuous hardening of a cooled liquid in such a way so as to avoid crystallization. Therefore one can assume that the formation of glass necessarily is a process of preventing crystallization. In contrast to crystalline solids, neither the ideal glass nor the amorphous material exhibits translational symmetry. The difference between a glass and the corresponding liquid or super cooled liquid may be conveniently demonstrated by the volume-temperature relationship (Fig. 3.1). The Fig 3.1 indicates that, the greater the cooling rate, the smaller the sample volume and the slower the crystallization and larger will be the possibility of glass formation. Liquids with small crystallization kinetic constants can thus form glasses directly from the melt. Due to the slow cooling a liquid from any temperature $T$, to the melting point of the crystal ($T_m$) will follow a path 'a'. However, when rapid cooling inhibits the crystallization, the V-T relationship follows path 'b' to produce a super cooled liquid. Upon further cooling to the glass transition temperature $T_g$ and when the viscosity of the super cooled liquid is approximately $10^{13} - 10^{14}$
Figure 3.1 Changes in glass volume on cooling. The line ABCD represents a substance that crystallizes at B. The line ABEF the glassy form of the same material.
poise, a break in the curve occurs at a point indicated by E. There is an arbitrary choice of the value of the viscosity that characterizes a glass, it is commonly taken as $10^{15}$ Poise. Below, $T_g$, a non-crystalline material is formed that exhibits a high viscosity. Here the atomic motions are retarded and the relaxation time exceeds the time generally taken for performing quantitative measurements.

Present views of the structure of glasses and amorphous materials are derived from the postulates of Zachreisen (1932). Zachreisen argued that since the mechanical strength of glass is of the same order as the strength of crystals, then the atoms in glassy materials are linked by forces that are essentially the same as these in crystals, the atoms must oscillate about definite equilibrium positions. As in crystals, the atoms in a glass form an extended three dimensional network, there is an absence of a sharp X-ray diffraction pattern beyond the second nearest neighbour distance, the glass network is not periodic on an extended scale - hence the term 'amorphous, or 'disorder' is most descriptive.

The alloys of chalcogenide glasses have a certain range of atomic percentages of each constituent in which they can be glassy and beyond this range they are either semi-crystalline or crystalline. It is therefore necessary that a glass forming region of a specific system, or a combination of systems, is mapped out systematically. Many small samples of specific compositions are prepared, reacted, quenched and their crystalline or amorphous nature is determined by critical
examination. The extent of glass forming region is slightly dependent upon quench rate or the amount of material used in the sample preparation.

The tendency of chalcogenide systems to form glasses, as well as the physical and chemical properties of the glasses, is determined by the character of the chemical bond between the atoms that make up the glass. An increased tendency to glass formation is possessed by chalcogenide compounds and alloys with predominantly covalent chemical bonds. This is attested by the positions of the main components of the chalcogenide glasses in the periodic system of the elements. They belong to groups IV-VII of neighbouring periods, and are compactly placed. This group also includes the elemental semiconductor germanium and silicon. When these elements interact, the ion bond component that hinders glass formation should be minimal.

Another factor that hinders glass formation in chalcogenide system is the metallization of the chemical bonds, which increases with decreasing number of the group of the periodic system. The metallization manifests itself in particular in a delocalization of rigidly directed covalent bonds. The delocalization of the bond in space is accompanied by smearing of the wave functions. Consequently the redistribution of the components of the glass in the softening temperature region becomes easier and the ability of the melts to become crystallized is increased.
Glassy alloys of Se-Te were synthesized as a rule from elemental substances of equal degree of purity. For this purpose, materials of 'very pure' grade (5N pure) were used. The total weight of the obtained glassy alloy was determined by studying its crystallizing ability. Glasses of low crystallizing ability can be synthesized in any amount. Easily crystallizing glasses can be synthesized in amounts $10^{-5}$ gm and less. The smaller the total weight of the melt, the higher the rate at which this melts can be cooled uniformly.

The synthesis was carried out in evacuated quartz ampoules followed by quenching in ice water. The exact proportions of high purity (99.999%) elements, in accordance with their atomic percentages, were weighed using an electronic balance with a least count of $10^{-4}$ gm. The materials were then sealed in evacuated quartz ampoules ($10^{-5}$ Torr). The ampoules containing the alloys of $\text{Ge}_{30}\text{Sb}_{20-x}\text{S}_{50+x}$ were synthesized at 700°C and were held at the same temperature for about 10 hour. The temperature of the furnace was raised slowly at a rate of 3-4°C/min.

During heating, all the ampoules were constantly rocked for better homogenization of the alloys. This was achieved with the help of a ceramic rod to which all the ampoules were tucked away in the furnace. Rotating the same rod after every five minutes interval of time did this. Thereafter, the obtained melts were cooled rapidly by removing the ampoules from the furnace and dropping into the ice cold water. Quenching allowed the glass to retain as much as possible, a
definite structure corresponding approximately to the structure of the melt at the synthesis temperature. The quenched samples were taken out by breaking the ampoules.

The vacuum sealing arrangement used for the preparation of glassy alloys consists of rotary and diffusion pumps for evacuating the ampoule, vacuum gauges for measuring the vacuum, hand torch, oxygen and LP gas cylinders for sealing the ampoule, which contained the material in desired proportions. A vacuum $\sim 10^{-5}$ Torr was maintained in the ampoule, while sealing it, using the above system.

Amorphous materials are often characterized by their diffraction pattern, which consists of a few broad haloes, rather than sharp Bragg reflections. Keeping in view, X-ray diffraction patterns of all glassy alloys were obtained by using powder technique on X-ray diffractometer. The diffraction curves of the prepared alloys did not show any peak, which confirmed that the material was in disordered state.

Glassy samples can also be characterized by DSC technique which records the heat flow as a function of temperature keeping the sample and reference isothermal to each other. Watson first gave the name in 1963. Calorimetry can be used to detect the enthalpy and specific heat changes, which accompany structural transitions. The Differential Scanning Calorimeters determine transition temperatures and provide quantitative data on reaction.
enthalpies, heat capacities and heat capacity changes during amorphous to
crystalline transformations. The scanning character of this technique provides a
'thermal spectrum' of characteristic temperatures, glass, transition temperature
\( T_g \), crystallization temperature \( T_c \) and crystalline melting temperature \( T_m \).

A large amount of information can be obtained from thermal spectra. The observation of a glass transition indicates the presence of a glassy phase, and
two glass transitions indicate phase separation with the two phases having
different glass transition temperatures. Phase separation is also indicated when the
glass transition temperature is invariant with composition. Cervinka et al. have
also demonstrated the glassy nature of ternary alloys quenched from the melt by
observing, thermally, the glass transition, and subsequent crystallization.

3.2 Thin Film Preparation:

The deposition techniques and its associated process parameters
have a characteristic effect on the nucleation- and growth - dominated
microstructure of a thin film and thereby its physical properties. Two-dimensional
materials of thickness ranging from angstroms to hundreds of micrometers can be
prepared by a host of so called thin film as well as thick film techniques. The later
methods involve the preparation of thin materials from a paste or liquid form of
the bulk materials. The two sets of techniques are used by Lakotos et al. for thin
film materials of different microstructures and associated properties [1].
There are several methods for the film deposition, which are classified as follows:

1. Physical vapour deposition technique (PVD)
2. Chemical vapour deposition (CVD)
3. Electrodeless or solution growth
4. Electrochemical deposition (ECD)

By combining PVD with CVD hybrid techniques such as reactive evaporation, sputtering and plasma deposition have been established. The physical term evaporation describes the phenomena when a surface atom which by thermal heating has gained a vibrational energy exceeding its binding energy, leaves the solid or liquid and inter the gas phase. Thin film preparation by evaporation involves the creation of vapours or clusters of atoms by heating a material. The transportation of vapours and subsequent condensation on a substrate maintained at low temperature than that of vapours. The temperature of the source is an essential parameter for determining the rate of evaporation.

The detailed explanation of PVD & CVD techniques is given in the corresponding articles. The electrical, structural and optical properties of films mainly depend upon the doping and deposition techniques.

In the present work we have used Physical Vapour Deposition Technique (PVD) for the preparation of the samples.
3.3 Physical Vapour Deposition Technique:

3.3.a Vacuum Evaporation:

The evaporation of a material requires that it be heated to a sufficiently high temperature to produce the desired vapour pressure. The rate of free evaporation of vapour atoms from a clean surface of unit area in vacuum is given by the Langmuir-Dushman kinetic theory equation

\[ \text{Ne} = 3.513 \times 10^{22} \frac{\text{Pe}}{(\text{MT})^{1/2}} \text{ [Molecules cm}^{-2}\text{ s}^{-1}] \]  

(3.1)

Where \( \text{Pe} \) is the equilibrium vapour pressure (in Torr) of the evaporant under saturated vapour conditions at a temperature \( T \) and \( M \) is the molecular weight of the vapour species. The vapour atoms traverse the medium and made to condense on a substrate surface to form a thin film. The rate of condensation or the deposition of the vapour atoms depends on the vapour-source-substrate geometry and the condensation coefficient on the surface under given physical conditions.

The vapour atoms are scattered by collisions with residual gas atoms in the vacuum system. The scattering probability is proportional to \( e^{-d/\lambda} \) where \( d \) is the source-substrate distance and \( \lambda \), is the mean free path of the gas atoms. In addition, the gas molecules impinge on the substrate surface at a rate given by equation (3.1) where of course the parameters \( \text{Pe}, T \) and \( M \) refer to the gas molecules at temperature \( T \). It was found from experiments that vacuum of the order of \( 10^{-5} \) Torr to \( 10^{-6} \) Torr is good enough for deposition of clean films except
1. Source

2. Evaporant (Material to be evaporated)

3. Substrate (On which film is to be formed or deposited and it should be chemically cleaned).

The simplest source for heating is resistance wires and metal foils of various size and shapes. Generally Tungsten (W) Molybdenum (Mo) and Tantalum (Ta) are used as a resistance wires and metal foils because they have high melting point and low vapour pressure.

The sources may be made in the laboratory by bending wires or sheets into the desired shape. Wetting of the metal foil surface by the molten evaporant is desirable in the interest of good thermal contact. But molten metal also lowers the electrical resistance of foil causing the temperature to drop. This problem is avoided with oxide coated foils.

The problem of finding non-reactive supports for materials evaporating above 1000°C can be overcome in these cases when vaporization temperature is near to the melting point of the evaporant. The materials such as Molybdes or Silicon, V and Si, reach vapourization temperature before they melt and hence can be sublimated. This allows evaporation from wires or foils of the film materials by direct resistance heating without contact with any foreign material. High purity, nickel and iron films have been prepared by this method.
Vapourization of the substances can also be done by electron bombardment instead of supplying energies by resistance or induction heating. A stream of electron is accelerated through field of 0.5 to 10 KeV and focussed onto the evaporant surface. Most of the Kinetic energy of the electrons is converted into heat and temperature above 3000°C may be obtained. It can be concentrated on the evaporating surface while other portions of the evaporant are maintained at lower temperature. Hence interaction between evaporant and support material are reduced.

3.4 Description of Vacuum Set Up Unit:

Vacuum evaporating requires a system with a known vacuum and it's residual gas analysis. A diffusion pump backed by a rotary pump continues to create a vacuum of about $10^{-6}$-$10^{-8}$ Torr in this film technology. This technology is widely because of there simplicity reasonable price, and high speed. By using special diffusion pump oil (e. g. poly phenylether), and minor altering to the system, ultra high vacuum (UHV) in the range $10^{-8}$ to $10^{-10}$ Torr can easily be obtained. The second most common system is based on sputter ion pumps backed by suckeem pumps and assisted by a Tisublimation pump, cryopump systems using clocked cycle, He-temperature probes are the new and the clean, but more expensive additions in the UHV field. It must be noted that each vacuum system has it's own character from the point of view of pumping characteristics and
residual gas composition. Further, each system may interact with a thin film condensation process in its own way.

Besides a vapour source, one requires numerous other accessories in the vacuum system. These include shutters, substrate heaters, a planetary system (for uniform deposition over large areas) and monitors and controllers for deposition rate and films thickness.

All the accessories must necessarily be made of materials compatible with UHV technology from the point of view of degassing and chemical reactions with the required vapours. The deposition rate is commonly monitored and controlled with the help of a quartz crystal oscillator. The film thickness is monitored by integrating the rate monitor signal or by other techniques such as an optical monitor (for non-metallic films). In view of their important role in obtaining films of desired properties a detailed understanding of the deposition accessories is essential.

For vacuum evaporation we are using HIND HIVAC vacuum coating unit model No 12 A4, for the preparation of the thin films. Fig. 3.2 shows the sketch diagram of vacuum coating unit. The description of this model, in brief has been given as follows

"HIND HIVAC" vacuum coating unit model No. 12 A4 can cover large number of laboratory applications like preparation of thin films for optical and electronic applications, preparation of specimens for electron microscope etc.
Figure 3.2 Block Diagram of Vacuum Coating unit.

1. Vacuum Chamber
2. Base Plate
3. Penning Gauge
4. Baffle Valve
5. Chimneys
6. Water coolant Arrangement
7. Silicon Oil
8. Heater
9. Pirani Gauge
10. Roughing Valve
11. Magnetic Isolation Trap
12. Blocking Valve
13. Rotary Valve
The basic unit consists of a cabinet containing a vacuum pumping unit together with the entire electrical component necessary for the coating process.

The vacuum chamber is fabricated from pyrex brand glass. When the chamber is placed on the base plate by means of a neoprene gasket.

A cooling water pipeline is attached to the outside of the chamber to prevent over heating, especially at the chamber window and to reduce the outgassing by circulating the water.

The chamber is evacuated by HIND HIVAC Model OD-114 oil diffusion pump and backed by a 200 litre per minute double stage gas ballast rotary pump V-belt driven from a 3/4" HP motor with overload protection. The effective speed of the pumping is 180 litre per second.

A model STA 6P3/STC 2P3 Pirani / Thermocouple – Penning joint gauge fully established is provided. This gauge, operates in conjunction with two Pirani two thermocouple gauge heads, are placed in the unit, one mounted in the rotary pump pipeline and the other in the chamber for measuring the temp. The penning gauge head is mounted to the chamber. The Pirani / Thermocouple gauge measures from 0.5 Torr to $10^{-3}$ Torr. (1 micron) and the penning gauge measures from $10^{-2}$ Torr (10 microns) to $10^{-6}$ Torr (0.001 microns).

Pirani/thermocouple gauge is used to measure roughing and backing pressure and penning gauge is used to measure fine pressures in the chamber. 230
VAC single-phase 50 Hz 15 amps is used for the purpose. Maximum Power Consumption about 3 KVA in full load condition.

There is a cool water circulation system at 15°C which keeps the system cool in full load condition at fuel consumption rate of about one litre / minute.

The rotary drive is useful for deposition of materials uniformly on large plane surface substrates. This comprises of a rotating work holder, which has a useful diameter of 6". The work holder ring is supported by three equally spaced ball bearings one of which is spring-loaded acting on the rim of the work holder. The work holder is rotated by a variable speed electric motor situated on a plate form inside the coating unit cabinet. The speed of the rotary drive motor is controlled by a solid state speed control fitted on the front hand side pillar.

This is used in conjunction with the rotary drive. This high tension discharge cleaning system consisting of radiant super pure aluminum electrode bar. The bar is shielded to avoid electron contamination of the substrate during discharge cleaning.

This source shutter plate is designed to cover any one of the off sector filament holders meant for sequential evaporating when a rotary drive is used. The shutter plate is attached to standard source shutter shaft when a rotary drive is used.
These filament holders are used in conjunction with rotary drive. They are designed to distribute uniform evaporating on a rotating plane substrate held in the rotary work holder ring.

The multifilament turret is designed to evaporate four different materials vertically below the center of the work holder ring without breaking the vacuum. There is no provision to evaporate from off sector to be used along with the rotary drive, so this gadget only is to be used with spherical work holder for multi layer depositions.

This thermal evaporating system consists of four positions vapour turret constructed in copper permitting current loading up to 100 amps. The low tension earth brush is in permanent contact with the rim of the turret low tension earth plate and low tension line electrode brush will make the contact when ever that evaporating source comes to the firing position. The turret that is supported on a circular plate positioned 3”, above the base plate (from base plate to filament) is rotated by external hand wheel. The movement is transmitted into the vacuum system via a ¼” Wilson shaft seal and a chain drive. The evaporating is carried out from the vapour source positioned vertically below the centre of the work holder ring. Each source can be adjusted to evaporating position by observing through the chamber window and that particular number of the source can be identified at the hand wheel indicator.
The radiant heater is fixed inside the chamber on top of the work holder ring. This can be easily installed and removed through the plug in type leads. This is capable of heating the substrate up to a temperature range of 250 degree to 275 degrees in about 30 minutes. The heater element in nichrome and has a power rooting of about 500 watts 120 V to 140 V one of the revolutions of the variac control is used and the circuit is fused at 5 amps to prevent over loading of the heater. Electrical connection is made via two loads fitted through the base plate.

Temperature measurement is made using a chronel alumel thermocouple in conjunction with 500°C meter mounted on the meter panel. The thermocouple leads are brought out the vacuum system via a multipin lead through in the base plate.

The electron gun is a vapour deposition source designed to produce thin films in high vacuum. The gun can achieve temperatures in excess of 3000°C. This is readily adequate to produce thin metallic and non metallic film of the refractory metals such as tungsten, tantalum and molybdenum.

The gun consists of three principle parts, a water cooled sample holder (Anode), a filament (cathode) and a shield. In operation the filament is resistively heated by a filament power supply to the point where it admits electrons. One end of the filament is connected to the shield. This prevents electron from being accelerated by and striking the shield. The sample holder is
kept at several K.V. position with respect to the filament an shield by high voltage supply. This causes the electrons which have been emitted by the filament to be accelerated towards and strike the sample in the sample holder on striking they give up energy that they gained during accelerations, heating the sample to the point where it evaporates. The shield prevents the evaporated materials from leaving the gun in any direction other than through the part made in the top shield. A power supply consisting of H.T. and L.T. with meters and controls will be supplementary with the gun.

With the help of the above coating unit we can achieve the pressure of about of the order of \(10^{-6}\) Torr.

This technique is used to deposit the metal and their oxide films. In deposition of metal films, the background temperature is kept as low as possible because the interaction of residual gases with evaporant affects the film properties. However, in reactive evaporating, high oxygen pressure is mentioned to produce fully oxide metal films. This technique is applicable in those cases where metal oxide cannot be evaporated directly because of complete or partial decomposition.

The reactive evaporating of metals or metal oxides on to substrates at moderate temperatures, produce amorphous or fully crystalline films whose stoichiometry is largely determined by the impingement ratio of the constituents. However, because of the differences in condensation cooling ratio, film composition is not the same as impingement ratio. In metal oxide, which has been
reactively evaporated, the deposition rates are small to ensure a high impingement ratio to increase the oxygen pressure, the existing studies pertain mostly to oxide, and reactive evaporation is applicable to other classes of compounds also.

The single component can easily evaporated with the help of resistance-heated wires or boat and finally the film is deposited on a substrate.

In this case multicomponent alloys or compounds are thermally evaporated. The composition may evaporate at different rate because of their different vapour pressure due to their different tendencies to react with support materials.

A satisfactory method to prepare alloys and compounds with precisely controlled composition is to evaporate each component from a separate source. The growth of the film can be controlled (thickness and growth rate) with the help of the thickness monitor and growth rate monitor the deposition of the film whose constituent have different vapour pressure. The film composition is accomplished by evaporating small quantity of the constituents in the desired ratio. Only one filament is used at a temperature (Sufficiently high) to evaporate the materials.

In the above case the evaporation of materials is only possible in the powder form and not in wire form. Flash evaporation is performed in vacuum of the order of $10^{-5}$ Torr. This technique has been used to prepare single phase pseudo binary compounds of different groups and multicomponent alloys.
The high intensity of the laser can be used for heat and vaporize the materials by keeping the laser source outside the vacuum system and focusing the beam on to the surface of a materials to be evaporated. But the disadvantage is, since the layer penetration depth is small (~100Å) evaporation takes place at the surface only. Non - Q - spoiled glass neodymium laser is used to deliver 80 to 150 J of energy per burst with duration of 2 to 4 m Sec.

Our study is concentrated on the Chalcogenide glasses system of the combination as Ge-Sb-S for measuring the optical constants at different annealing temperatures. The samples of the different combinations will be prepared by quenching technique. The combination of samples will be as follows: -

\[
\begin{align*}
\text{Ge}_{20}\text{Sb}_{20}\text{S}_{50} \\
\text{Ge}_{30}\text{Sb}_{16}\text{S}_{54} \\
\text{Ge}_{30}\text{Sb}_{12}\text{S}_{58} \\
\text{Ge}_{30}\text{Sb}_{08}\text{S}_{62} \\
\text{Ge}_{30}\text{Sb}_{04}\text{S}_{66}
\end{align*}
\]

Chalcogenide glasses in the systems \(\text{Ge}_{30}\text{Sb}_{20-x}\text{S}_{50+x}\) where \(x = 0, 4, 8, 12\) and 16 was prepared by quenches technique. Materials (99.999% pure) was weighted according to their atomic percentages and sealed in quartz ampoules (length \(\approx 6\) cm.; internal diameter \(\approx 8\) mm.) in a vacuum of \(10^{-5}\) Torr. The sealed ampoules were kept inside a furnace, where the temperature was raised to \(850^\circ\text{C}\) at the rate of 3-4\(^\circ\text{C}\) per min. The ampoules was frequently be rocked for 10 hours.
at a maximum temperature to make the melt homogeneous. The quenching of the sample was done in ice water.

Thin film of glassy alloys of thickness $3000\text{A}^\circ$ were prepared by the vacuum evaporation technique, in which the substrate were kept at room temperature ($36^\circ\text{C}$) at a base pressure of $10^{-6}$ Torr using a molybdenum boat. The films were kept inside the deposition chamber for 24 hours to achieve the metastable equilibrium as suggested by Ovshinky [2]. The thickness of the film was measured using a single crystal thickness monitor. A JASCO, V-500, UN/VIS/NIR computerized spectrophotometer is used for measuring optical absorption, reflection and transmission of these films. The optical absorption, reflection and transmission were measured as a function of wavelength.

The glassy alloys prepared were ground to make fine powder for the thermal measurement. Glassy alloys as well as thin films were characterized using X-ray diffractometer (Thermo Electron Corporation, Model ARL X’TRA) at scan rate of 2 deg/min. No prominent peak was observed in XRD of bulk samples as well as thin films, which verifies their amorphous nature as shown in Fig.3.3. The homogeneity and correct compositions of all the alloys and thin films were determined by means of scanning electron microscope (Zeiss, Model EVO 40). Film compositions were different from by bulk samples by up to $\sim 3\%$.

Thin film of glassy alloys was exposed in a specially designed sample holder under a vacuum of $10^{-4}$ Torr with different temperature below the
Figure 3.3 X-ray Diffraction pattern for different compositions of the samples (a) Ge$_{30}$Sb$_{20}$S$_{50}$ (b) Ge$_{30}$Sb$_{16}$S$_{54}$ (c) Ge$_{30}$Sb$_{12}$S$_{58}$ (d) Ge$_{30}$Sb$_{08}$S$_{62}$. 
crystallization temperatures for different interval of time. The temperature was measured with calibrated chromel alumel thermocouple mounted near the thin films. The samples were annealed slightly above the room temperature at 50°C, 77°C and 98°C for four hours. The same measurements were repeated for all the series of the sample to see the annealing effect on the samples. [3 – 6]

3.5 EXPERIMENTAL DETAILS OF CONDUCTIVITY MEASUREMENTS:

A specially designed metallic sample holder (Fig. 3.4) was used for the measurement of D.C. conductivity in a vacuum ~ 10^{-3} Torr. The films were mounted on a base plate of copper (size 3 cm x 3 cm). Copper clips were used for the electrical contacts. Electrical connections from the sample were taken using Teflon insulated wires to the two Teflon insulated feed. A copper rod holding substrate holder had a heater (35 watt or as required) wound around it. Sample temperature was measured by a copper – constantan thermocouple. The cryostat was provided with a quartz window through which the light could be shone on the sample. The leakage current through the feed through (BNC connectors, vacuum tight) was below the measuring limit (10^{-14}A) of the electrometer used. The leakage current through the glass substrates was also measured by depositing two electrodes of indium at a separation of 0.2 to 0.5mm. The leakage current was again found to be less than 10^{-14}A which ensured the current measurements through the amorphous films deposited on the glass substrates. To avoid the noise signal, a D.C. voltage was used for the heater inside the sample holder particularly current measurements in pA range.

The sample holder contains two parts. The upper part consists of two electrodes and an evacuation port while the lower part contains the outer covering and a quartz window.

The sample can be mounted on the upper portion of the sample holder which having a heating arrangement. At the end of the two electrodes, two
Figure - 3.4 Sample holder used for measurements of d.c conductivity of thin films at different temperatures in vacuum.
UHF connectors were used for the electrical connections of the sample. Canthal were wound as heating element on the outer covering of the sample holder assembly. Heating element was covered with plaster of Paris beads in order to avoid heat losses due to radiations.

A calibrated copper constantan thermocouple was mounted very near to the sample to measure the temperature of the sample. An O-ring was provide between the two parts of the sample holder for proper evacuation inside the chamber. A rotary pump was used to obtain a vacuum of \( \sim 10^{-3} \) Torr.

For the conductivity measurements the samples used are in the thin film form on the quartz plate having diameter \( \sim 6\text{mm} \) and thickness \( \sim 5000\text{Å} \).

Pure samples were used to avoid any electrode migration at high temperature. Several temperature had been chosen between the glass transition and melting temperatures for the isothermal annealing. Different samples were taken for each temperature of annealing. The temperature was obtained initially at a faster heating rate and then maintained for quite some time until saturation in resistance is reached. The amorphous to crystalline transformation is studied by measuring the d.c. conductivity \((\sigma)\) as function of time (1-2 min. intervals) at various annealing temperature.

The resistance was measured for conductivity measurements by using Keithley electrometer (model 614). The temperature was measure using a calibrate copper constantan thermocouple. The least count of this digital electrometer is 0.01 Gohm in the highest resistance range. The temperature was maintained constant by applying a constant voltage to the heating element.
REFERENCES


