CHAPTER 3

EXPERIMENTAL METHODS

3.1 INTRODUCTION

Experimental techniques include choice of the substrate and its cleaning, preparation of the film and measurement of film thickness. Deposition of film is by one of the various processes under broad classification of physical and chemical methods. Substrate on which film is formed is chosen according to the characterization and the type of application. Film preparation, pressure measurement and thickness measurement are outlined as part of this chapter.

3.2 CHOICE OF THE SUBSTRATE

Substrates play an important role in semiconductor electro deposition and thin film requires a substrate to support itself. The substrate provides necessary mechanical strength and rigidity needed for the film and it has adequate thermal ability to ensure at room temperature that can withstand high temperature. The function of the substrate is to provide the base onto which the thin circuits are fabricated and various thin film multi layers are deposited. To form thin film with distinct electrical parameters, the substrates must be smooth and flat otherwise the properties may be affected. Therefore in choosing a suitable substrate, in addition to considering the need to provide the mechanical support to the film, due consideration must be given to the possible influence of substrates and properties of the film.
Commonly used substrate materials for polycrystalline thin film circuits include alumina, glass, silicon and metals, beryllium oxide based ceramic and aluminum nitride. When the films are deposited on glass, electrical and optical measurements are not disturbed by an underlying layer and thus are easier to interpret in a suitable way.

3.3 REQUIREMENTS OF THE SUBSTRATE

In order to produce defect free films, the substrate must satisfy the following requirements.

The coefficient of thermal expansion of substrate must be similar to that of deposit film to minimize mechanical and residual stress of the film. Mechanical strength is required to enable the substrate to withstand vigorous processing. Thermal conductivity is required to remove the heat, enabling the realization of the circuits with high component densities. Low porosity is required to prevent the entrapment of gases, which cause film contamination. The substrates must act as good insulators at room temperature ie, it must have electrical resistance ($>10^{14}$ ohm cm) and moreover substrate must have good uniformity and surface smoothness. Of all these glass is found to possess all the requirements and is economically and widely used, as described by Aicha et al (1998).

3.4 CLEANING OF THE SUBSTRATE

Substrate cleaning in thin film technology is an important step prior to deposition. It is necessary to remove the contaminants that would otherwise affect the properties of the film. Cleaning involves the removal of contaminants without damage to the substrate. As pointed by Joy George (1992), the bond between the substrates is broken while cleaning, and the contaminants are set free from the substrates. Presence of contaminants can
affect the morphology, electronic properties, nucleation and substrate-film interface. Expected contaminants include fingerprints, dust, lint particles and oil. Before designing the cleaning process, the physical properties such as porosity, thermal expansion, conductivity and chemistry of the substrate must be carefully examined. The energy required to break these bonds can be supported by chemical salvation, thermal or mechanical processes.

The procedure for cleaning the glass substrate involves the following processes,

i) Ultrasonic Cleaning

This cleaning is assisted by ultrasonic agitation in which jetting, accompanies the collapse of bubbles generated by cavitations near the surface. The substrates are rinsed with distilled water and placed in an ultrasonic cleaner where they are agitated for 30 min in a solution of detergent and distilled water. This removes oil, grease and dirt.

ii) Solvent Cleaning

Solvent cleaning is employed to dissolve contamination. This cleaning takes place when the solvent vapors condense on the substrate by placing in an isopropyl alcohol for 30 min.

iii) Hot Air Cleaning

Heating the substrates may remove the volatile impurities. The temperature is chosen according to the melting point of the substrate and is heated in a hot air oven for 1 hr at 100°C.
3.5 THIN FILM DEPOSITION TECHNIQUES

Thin films can be produced onto metallic or non-metallic supports by several deposition techniques as described by Holland (1956), Glang (1970). The choice of a particular deposition technique depends on substance to be deposited, thickness, nature of the base material and film structure. Deposition technique and its associated parameters have characteristic effect on the nucleation and growth dominated microstructure of the film and thereby on the physical properties of the film (Kasturi Lal chpora and Suhit Ranjan Das 1983). The two categories for thin film processes are chemical and physical methods.

3.5.1 Chemical Methods

According to Maissel (1966) the two most important chemical methods are electrodeposition and chemical vapour deposition.

3.5.1.1 Electrodeposition

There are basically two technologies for electro deposition: electroplating and electro less plating.

In the electroplating process the substrate is placed in a liquid solution called electrolyte. When an electrical potential is applied between a conducting area on the substrate and a counter electrode (usually platinum) in the liquid, a chemical redox process takes place resulting in the formation of a layer of material on the substrate and some gas generation at the counter electrode.

In the electro less plating process a more complex chemical solution is used, in which deposition happens spontaneously on any surface which forms a sufficiently high electrochemical potential with the solution. This process is desirable since it does not require any external electrical
potential and contact to the substrate during processing. Unfortunately, it is
difficult to control uniformity and thickness of the film.

3.5.1.2 Chemical Vapor Deposition (CVD)

In this process, the substrate is placed inside a reactor to which a
number of gases are supplied and the fundamental principle of the process is
that a chemical reaction takes place between the source gases. The product of
that reaction is a solid material which condenses on all surfaces inside the
reactor. The two most important CVD technologies are the Low Pressure
CVD (LPCVD) and Plasma Enhanced CVD (PECVD). The LPCVD process
produces layers with excellent uniformity of thickness and material
characteristics. The main problems with the process are the high deposition
temperature (higher than 600°C) and the relatively slow deposition rate. The
PECVD process can operate at lower temperatures (down to 300°C) supplied
to the gas molecules by the plasma in the reactor. However, the quality of the
films tends to be inferior to processes running at higher temperatures.
Secondly, most PECVD deposition systems can only deposit the material on
one side of the wafers on 1 to 4 wafers at a time whereas LPCVD systems
deposit films on both sides of at least 25 wafers at a time.

3.5.2 Physical Methods

Physical methods cover a number of deposition technologies in
which material is released from a source and transferred to the substrate. The
two most important technologies are sputtering and vacuum evaporation.

3.5.2.1 Sputtering

The ejection of atoms from the surface of material by bombardment
with energetic particles is called “sputtering”. The sputtered atoms condense
on the substrate to form a thin film. This ejection process known as
sputtering, takes place as result of momentum transfer between the impinging ions and the atoms of the target surface.

There are wide variety of sputtering techniques used to deposit thin films for use in magnetic storage media (cassette tapes, computer discs), optical thin films and microcircuits

1) Diode sputtering
2) Magnetron sputtering
3) RF sputtering, and
4) Ion beam sputtering.

3.5.2.2 Vacuum evaporation

In general, there are three steps in vacuum deposition process:

1) Creation of vapor from the source material
2) Transformation of vapor from source to the substrate
3) Condensation of vapor onto the substrate surface to form a thin film.

There are two reasons for this process to be conducted in vacuum:

1) The process of evaporation involves significant amounts of heat, if oxygen were present in the material; any reactive metal would form oxides.
2) Collisions with gas molecules during the transport of evaporant from source to substrate would reduce the net deposition rate significantly, and would also prevent growth of dense films.
Upon arrival at the substrate, evaporated material condenses on the substrate in a complex sequence of events that determine physical properties of the deposited film. The steps in the growth of thin films are generally referred to as nucleation and growth. In nucleation, the atoms and molecules (called ad atoms) which arrive at the surface lose thermal energy to the surface, and the surface absorbs that energy. Depending on the amount of thermal energy the ad atoms and the surface have, the ad atoms move on to the surface until they lose the thermal energy (referred to as Adam mobility). As nuclei continue to form; the film grows into a continuous sheet covering the substrate. Chemical interactions between ad atoms and the surface determine the strength of the bond between the film and substrate. Once a few monolayers of evaporant have condensed on the substrate, the film continues to grow in thickness as if the entire substrate were made of the material being deposited. During the growth of the film the microstructure of the film is developed and this microstructure may be described in terms of grain size, orientation, porosity, impurity content, and entrained gases.

Normally, vacuum deposition processes are selected over other processes to achieve the following desirable properties:

1) High chemical purity.

2) Good adhesion between the thin film and substrate.

3) Control over mechanical stress in the film.

4) Deposition of very thin layers, and multiple layers of different materials.

5) Low gas entrapment.
The parameters that are controlled during deposition to achieve specific goals are:

1) Kinetic energy of the ad atoms.
2) Substrate temperature.
3) Deposition rate of the thin film.
4) Augmented energy applied to the film during growth.
5) Gas scattering during transport of the evaporant.

By varying these parameters thin films of a given material that have different mechanical strength, adhesion, optical reflectivity, electrical resistivity, magnetic properties and density can be deposited.

The following are the advantages in this process:

1) Uniform distribution over large areas
2) No compositional gradients across substrate
3) No need to break vacuum for source changes
4) Large selective area deposition due to high energy activation
5) Safety.

There are several methods by which heat can be delivered to the material to cause vaporization:

1) Electric resistance heating
2) Laser ablation
3) Arc evaporation
4) Electron beam heating.
5) Flash evaporation
**Electric Resistance Heating**

Evaporation of material by electric resistance heating is the easiest of all thermal evaporation techniques. In a vacuum environment the material (which may be an elemental metal, an alloy, a mixture or a compound) is heated to become vapor. Low voltage, high current (typically 10 to 40 VDC, 1 to 10 amps) power is brought into the vacuum vessel using electrical power feed through and the electrical power is passed through a filament which is in intimate contact with the material. Filaments are often heated to 1000 to 2000° C. A material requirement for efficient thermal evaporation is that the charge has an appreciable vapor pressure at the operating temperature of the filament.

**Electron Beam Evaporation**

In this process, a beam of energetic electrons generated from a heated filament supplies the thermal energy to evaporate the material. There are several variants of the electron beam evaporation process. All electron beam evaporation systems have an anode (biased positively) and a cathode (either grounded, or biased negatively with respect to the anode). Self accelerated and work-accelerated are the two divisions of electron beam evaporators and in the work-accelerated scheme, electrons emitted from a heated tungsten filament are attracted to the charge material by an applied high voltage bias (10- 40 kV DC).

**Arc Deposition**

High current, low voltage electric arcs are used to produce evaporation for thin film coatings. There are several techniques used to control the arc, including use of electrically insulating hearths, electrostatic, and magnetic constraints. Arc deposition has been demonstrated to produce
thin films having high densities and excellent adherence to the substrate. Normally the arc process is conducted in a UHV environment, but partial pressures of reactive gases, such as oxygen and nitrogen have been used to deposit metal oxide and nitride thin films. High deposition rates in the range 50 to 500 Å/sec have been reported for the arc deposition process.

**Laser Ablation**

High energy density pulsed laser beams have been used to deposit thin films of a variety of elements, alloys and compounds. In this process, a laser source, external to the vacuum vessel generates a beam which is focused, to a viewport and impinges on a target within the vacuum vessel. Sufficient energy is generated to blast (ablate) material from the surface of the target. This ablated material consists of neutral atoms, ions, clusters of atoms and macro particles. The amount of material deposited per laser pulse is very consistent, allowing one to accurately deposit films of a specific thickness. The deposition rate is low compared to other techniques (electron beam evaporation and sputtering, for example). Some of the thin films that have been deposited using laser ablation include super conducting thin films, ceramic coatings, and amorphous metallic layers.

**Flash Evaporation**

It is a rapid evaporation of multi component alloy or compound which tends to distill fractionally, and obtained continuously by dropping fine particles of material onto hot surface so that large discrete evaporation occurs. Constant composition of the film can be obtained by this method.

**3.6 VACUUM COATING UNIT**

The photograph of “HIND HIVAC” coating unit (12A4D) used in the present work is shown in Figure 3.1.
The unit consists of three main parts mainly

(1) Pumping system
(2) Surface coating chamber apparatus
(3) Electrical equipment with apparatus

Figure 3.1 Photograph of “HIND HVAC” coating unit
Pumping System

The vacuum chamber can be evacuated by a three stage oil diffusion pump backed by a double stage gas ballast rotary pump capable of evacuating 200 litres/min.

Pressure and Gas Flow

In vacuum work, pressures are almost measured in millimeters of mercury, or Torr. One Torr is just the pressure necessary to support a column of mercury with a height of one millimeter

1 atmosphere = 101 kPa = 760 Torr

There are two pressure regimes working with vacuum systems, and gases behave differently in each regime. First, the viscous flow regime, describes the case where gas flows as a fluid, in which the mean free path of the gas molecules is much smaller than the dimensions of the apparatus. Second, the molecular flow regime, describes the high-vacuum case, where the mean free path is much longer than the characteristic dimensions of the apparatus. In this regime, gas molecules interact almost entirely with the walls of the chamber, acting independent of each other.

Gas flow in either regime is measured in Torr liters/sec, which is equivalent to mass per second. The conductance of a tube describes how much gas flows through the tube for a given pressure differential between the ends. If $Q$ is the mass flow, $P_1$ is the pressure at the input of the tube, and $P_2$ is the pressure at the output, then the mass flow is given by

$$Q = (P_1 - P_2)C$$  \hspace{1cm} (3.1)

where ‘$C$’ is the conductance of the tube.
**Vacuum Pumps**

Mechanical pumps feature multiple stages, specialized low-vapor-pressure oil sealants, and electric motors. Modern mechanical pumps can often attain base pressures of a few milli Torr or a few tens of milli Torr, though below 100 milli Torr the oil used in them will often leak back into the chamber being pumped on and this process is called as back streaming. Back streaming can be eliminated by placing a trap or high-vacuum pump between the mechanical pump and the chamber. Mechanical pumps are seldom operated below 100 milli Torr, and are often referred to as roughing pumps. The most common and reliable high-vacuum pumps in use are turbo molecular pumps which are used to achieve even a moderate vacuum of $10^{-2}$ Torr. It consists of very high-speed fans, whose blades are moving at speeds comparable to the speeds of gas molecules.

Turbo pumps are capable of sustaining very high compression ratios, the ratio of the gas pressure at the output to that at the input. Typical compression ratios are on the order of 10^7 for air, for an outlet pressure of 100 milli Torr. This low outlet pressure is maintained by a mechanical pump, which acts as both a roughing pump for the system and a backing pump for the turbo. One advantage of using a turbo pump in conjunction with a mechanical pump is that the turbo pump’s compression ratio depends strongly on the molecular weight of the gas being pumped. Because the oils used in mechanical pumps typically have very high molecular weights, the compression ratio across the turbo pump for these oils is considerably higher than 10^7, and the turbo pump effectively blocks any back streaming from the roughing pump. Speeds for turbo pumps are usually independent of the type of gas being pumped. Turbo pumps are specified by their speed, and the small turbo pump used in this lab has a speed of 80 l/s.
Vacuum Chamber

Two things that limit the level of vacuum in any experiment are leaks and out-gassing. Leaks are just poor seals that allow air to enter the chamber from the outside atmosphere. Out-gassing refers to sources of gas “stored up” inside the vacuum chamber and released slowly into the vacuum. A cooling water pipeline is coiled on the outer wall of the chamber to prevent over-heating, especially at the chamber windows. The oil diffusion pump is connected to the coating chamber, which permits the diffusion pump to be kept under vacuum and at operating temperature when the coating chamber is at atmospheric pressure.

Pressure Measurement

Just as different pumping schemes are used in viscous and molecular flow regimes, different methods of measuring the pressure are used in different ranges as well. Thermocouple gauge is used for measuring pressure between 2 to 10 milli Torr, and an ion gauge in the molecular-flow regime. A thermocouple gauge consists of a filament and thermocouple in contact with each other. There is a range of pressure, approximately 10 milli Torr to 2 Torr, where the thermal conductivity of the gas depends on the pressure. If a known amount of heat is dissipated in the filament, then its temperature, as measured by the thermocouple, will depend on the rate of heat lost to the surrounding gas. The gauge, the filament and the thermocouple, are enclosed in a plug attached to the chamber. The controller supplies power to the filament and performs the necessary conversion of thermocouple temperature to pressure, displaying the result on its front panel. These types of gauge cease are useful below a few milli Torr, where the thermal conductivity of the gas is negligible.
Very low pressures can be measured using an ion gauge known as penning gauge. An ion gauge consists of a filament (cathode), a positively charged grid (anode), and a negatively charged collection wire. Electrons boil off the filament by thermionic emission and are accelerated towards the grid. On the way to the grid, they collide with atoms in the surrounding gas, producing ions. These positively-charged ions then go to the collection wire, and the resulting current in the collection-wire circuit is proportional to the gas pressure. This proportionality constant is different for different gases, because different gases have different ionization potentials.

**Electrical Equipment**

Primary current to the transformer is indicated on 0-10amps ammeter. L.T secondary current is indicated on 0-200 amps ammeter.

**Thickness Measurement (Theory)**

Thickness is one of the most important thin film parameters since it largely determines the properties of the film. Thickness of the film was measured by employing quartz crystal monitor. Methods of monitoring thickness can be divided into several groups, including gravimetric, optical, electrical, and magnetic. Monitoring methods are very important because they allow the preparation of thin film of selected thickness.

The quartz crystal monitor utilizes the thickness shear mode of piezo-electric quartz crystal. In this, the major crystal surfaces are antinodal and mass added on either one or both sides shifts the resonance frequency irrespective of thickness, density, elastic constants, or stiffness of the added material. A $35^\circ 20'$ quartz crystal cut, called AT cut is generally used for the monitor because of its low temperature coefficient ($+5 \times 10^{-6}$ between
-20 and +60°C) for the resonant frequency. The frequency of the fundamental resonance of a thickness made for an AT cut crystal is given by

\[
f = \frac{1c^{1/2}}{2d\rho_q^{1/2}} = \frac{N}{d} = \frac{1670}{d} \text{mmKc/sec}
\]  

(3.2)

where \( d \) is the crystal thickness, \( \rho_q \) is the density, \( C \) is the shear elastic constant and

\[
N = \frac{c^{1/2}}{4\rho_q^{1/2}} = 1670 \frac{\text{mmKc}}{\text{sec}}
\]  

(3.3)

Warner and Stockbridge showed that a change in frequency due to a deposit of mass \( m' \), added to the area \( A' \) of the antinodal surface of a mechanical resonator, is given by,

\[
\Delta f = -f \frac{km}{\rho d Ad}
\]  

(3.4)

where the constant \( k=1 \) and then negative sign implies a decrease in the frequency.

Combining (3.2) and (3.4)

\[
\Delta f = -f \frac{km}{N\rho_q A} = -C_f \frac{m}{A} = C_f t \rho_{film}
\]  

(3.5)

where \( C_f = \frac{f^2k}{N\rho_{film}} \) is a constant of the crystal and \( m=At\rho_{film} \) assuming a uniform film thickness \( t \) and a constant density \( \rho_{film} \). Thus \( t = \frac{\Delta f}{C_f \rho_{film}} \) yields average film thickness.

Any deposit can easily be removed by dissolving the under layer in NAOH solution, and the same crystal may be used again. The sensitivity of
the crystal does not increase appreciably by depositing over larger area, except the conductive coating that increases the active area larger than the electrode. For the deposit covering smaller areas compared to electrode area, the sensitivity of the mass decreases slightly.

The standard method of operation of an AT-cut crystal is by perpendicular excitation using metal electrodes on the central area of each face. The crystal is operated at series resonance where parallel capacitance has a smaller effect. However, the capacitance should be kept small to maintain high frequency stability and a high Q value. The maximum sensitivity of a quartz crystal monitor is limited by variations in the crystal frequency due to the temperature, oscillator drive level and changes in the oscillator circuit. Water cooling of the crystal holder can easily be incorporated and may be necessary for excessive heating due to lengthy deposition times from extended sources. The crystal monitor is used to monitor the deposition rate and to control the evaporation rate from the vapor source.

3.7 PREPARATION OF Cu$_2$S THIN FILM

Vacuum evaporation is simple and the most widely used technique for synthesizing high purity semiconductor films with the help of Hind High vacuum coating unit. Copper sulphide powder (99.99% pure) obtained from Sigma Aldrich Company, India was used as the source material and placed in the molybdenum boat of (200 amps) and heated with high current by energizing transformer. The transformer was capable of supplying 150 amps at 20 volts that is necessary for heating the molybdenum sources used for evaporation purposes. The evaporant material was carefully degassed at lower temperature for about 30 min with the shutter closed. The substrate to source distance was optimized to be at 18.1 cm inside the vacuum chamber. Rotary drive was employed to maintain uniformity in film thickness. Constant
rate of evaporation 3Å/sec was maintained throughout the sample preparation. Thickness of the film was measured by using quartz crystal monitor. Temperature measurement was made using Chromel-Alumel in conjunction with a digital meter mounted on the front panel.

Cu$_2$S thin films of different thickness were deposited on properly cleaned flat glass substrate under the pressure of 10$^{-6}$ Torr by slowly varying the current. During evaporation, copper sulphide thin films were formed in black color. The adhesion of the film to the substrate seems to be extremely good.

3.8 FABRICATION OF Cu$_2$S THIN FILM CAPACITOR

The capacitor was formed on a substrate with dielectric layer in between the two metal electrodes (Al) so as to form Al- Cu$_2$S-Al (MSM) Structure.

Preparation of Mask

Mask has been immensely used in the fabrication of MSM structure. The electrode and dielectric layer masks were prepared from brass and thin mica sheets respectively. The brass masks of precise dimension with vertical edge have been prepared by photolithographic technique.

Cleaning of Mask

The masks should be cleaned with acetone to remove organic contaminants in order to avoid the formation of defects in the films. When the masks are in contact with the substrates any contaminant on the masks affects the film growth and may give rise to the development of weak spots in film structure.
Electrode Material

Electrode should adhere well to the substrate to form stable structure. The electrode material should not react with the dielectric film and must have a low dielectric resistance. Generally metals like gold, silver, aluminum, titanium, lead and tin has been used as electrode materials. Of this, gold, silver and copper have very low resistance but their adhesion to the substrate is poor. Titanium, lead and tin have good adhesion but offer high resistance. Only Al is used to posses both qualities and has been used for electrode deposition in the present work.

Electrode Deposition

Aluminum (99.99% purity) obtained from Aldrich chemicals, USA, was evaporated at a pressure of $10^{-5}$ Torr from a helical tungsten filament through brass masks to form bottom as well as top electrodes. The required structure of the electrode was attained with the aid of brass masks. The electrode shapes and the final MSM structure is shown in Figure 3.2.

Figure 3.2  (a) Top electrode (b) Dielectric layer ($\text{Cu}_2\text{S}$) over the top electrode (c) bottom electrode (d) final MSM structure
3.8 SUMMARY

There are many factors that influence the growth processes and modify the real structure of the film. The properties of thin films are largely determined by the growth conditions and deposition methods. Different thicknesses of Cu$_2$S thin film prepared by vacuum evaporation method are characterized for their structural, compositional, electrical and optical properties.