Chapter II

EXPERIMENTAL TECHNIQUES

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A general discussion of the experimental techniques used in this field of studies is presented in this chapter. It includes the techniques of synthsizing the alloys and compounds and of their crystal growth, preparation of thin films and measurement techniques of electrical and optical properties, X-ray diffraction etc.

I. TECHNIQUES FOR CRYSTAL GROWTH :

1.1 Synthesizing the compound or alloys :

For synthesizing a compound or an alloy of normal metallic components, the starting materials are first usually mechanically mixed in the solid state and then subjected to reaction in molten state in vacuum. In the present study an arrangement for rotating and rocking the ampoule containing the molten charge was used with a suitable horizontal furnace. This mixing unit is shown in Figure - 1. A ceramic pipe is passed centrally through the horizontal furnace. Its one end is fitted to the shaft of the motor of 1 rpm. The other end is clamped in a detachable chuck. A quartz ampoule of length nearly 20 cm and inner diameter 2 cm containing the material and sealed under a pressure of 10^{-4} to 10^{-5} torr is kept centrally inside the ceramic pipe of the mixing unit. The maximum temperature inside the furnace core is kept about 100°C above the melting point of the material. The temperature is measured and controlled (within ± 5°C) with a proportional temperature controller. The temperature is sensed with a chromel p alumel thermocouple. The rotation cum rocking of the quartz tube gives stirring effect to the molten charge. For thorough mixing and reaction of the charge, this treatment is continued for 2 to 3 days. The molten charge is then slowly cooled to room temperature.

1.2 Crystal growth :

Crystal growth is a complex process which usually takes place by a phase change and it can broadly be categorised as follows :

1. Solid state growth : Solid-Solid phase transition.
2. Melt growth : Liquid-Solid phase transition.
3. Vapour growth : Vapour-Solid phase transition.

Crystallization from melt is the most widely used method for crystal growth, mainly due to the higher growth rates obtainable and because it is easily susceptible to modifications. Also chances of chemical contamination are reduced compared to other methods. All the basic techniques are variants in the way materials can be crystallized in rods, crucibles, boats or tubes. Thus the Czochraslki technique involves controlled crystallization from a crucible by pulling the melt whereas the Kyropoulos technique does not involve pulling but crystallisation onto a seed-crystal in a crucible. Zone melting is the generic term for a series of techniques in which a molten zone (or zones) is formed and traversed along a bar so as to produce progressive melting and freezing. The horizontal Bridgman method involves the progressive crystallization of molten material in a boat or tube whilst the Stockbarger (Vertical Bridgman) technique is the vertical equivalent of the lateral process$^{(1)}$.

Principles of melt growth are based on cooling of a liquid (i.e. melt) to solidification in a controlled manner. Crystal growth from melt involves control of heat transport together with solute transport in case of alloys.

Bridgman - Stockbarger technique is capable of producing large size crystals from thin rods to ingots of several cms in diameter. The Bridgman crucible is usually a tube of circular cross section with a tapered shape formed at one of the ends. The tapered end leads through the negative temperature gradient thereby effecting the charge from the liquid to solid state and it provides conditions for single nucleation event required to grow subsequently as a single grain through the rest of the material as it solidifies. The Stockbarger-Bridgman vertical furnace is divided into two halves, the temperatures of which can be varied independently and hence suitable temperature gradient can be obtained. The lowering of the ampoule is controlled by a reduced gear mechanism motor. The lowering speed could be varied in the range : 4,8,10 and 15 mm/hr. using this arrangement. The set up used in the present work is shown in Figure - 2.

II. THIN FILMS :

Modern day technology requires several types of thin film for a variety of applications. The films can be single or multilayer coatings on suitable substrates of different shapes and sizes.

The basic steps involved in a thin film deposition techniques are :

(a) Creation of material to be deposited in an atomic, molecular or particulate form prior to deposition.

(b) Transport of material to the substrate in the form of a vapour stream, spray etc.

(c) Deposition of the material on the substrate and film growth by nucleation and growth process.

Thin film deposition techniques have been broadly classified into four main categories :

1. Physical Vapour deposition (PVD).
2. Chemical Vapour deposition (CVD).
3. Electroless or solution growth deposition.
4. Electro Chemical deposition (ECD).

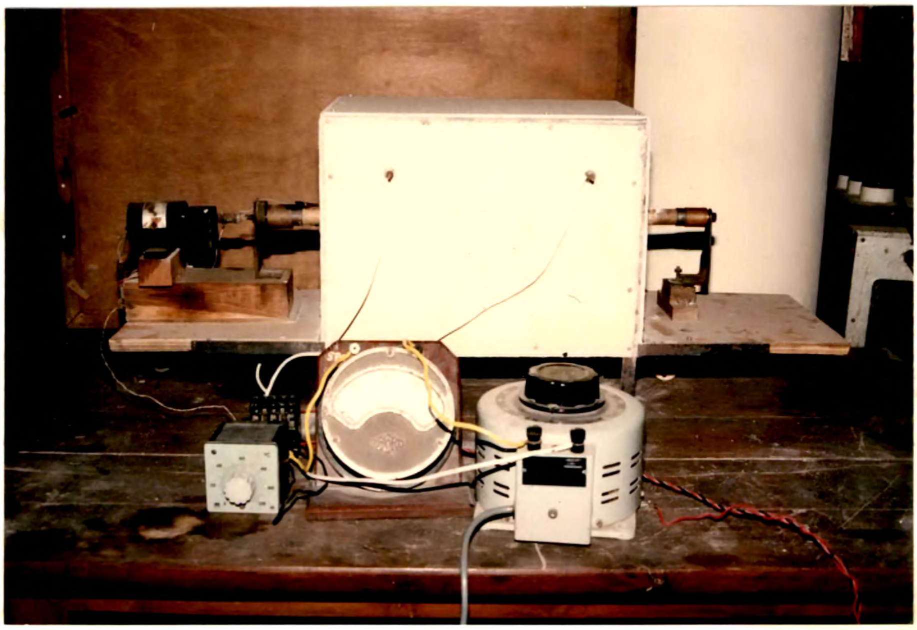

FIGURE - 1 : Alloy mixing unit.

FIGURE - 2 : Bridgman Furnace.

By combining PVD and CVD, hybrid techniques such as reactive evaporation/sputtering and plasma deposition have also been developed. The PVD technique has been used in this investigation.

PVD techniques are further classified into :

(i) Thermal evaporation.

(ii) Electron beam evaporation.

(iii) Molecular beam Epitaxy (MBE).

(iv) Activated Reactive evaporation (ARE).

(v) Ion plating.

2.1 Thermal evaporation :

It is one of the well known PVD techniques and the most widely used one. Large variety of materials (metals and semiconductors) can be evaporated and deposited on different substrates.

In the thermal evaporation, the material is created in a vapour form by means of resistive or RF heating. On heating a material in vacuum it evaporates at a rate given by the well-known Langmuir-Dushman equation. The vapour atoms are transported through vacuum and get deposited on the substrates. Only at pressures $\leqslant 10^{-5}$ torr, the mean free path of molecules becomes large so that the vapour beam reaches the substrate nearly unscattered.

A variety of sources are used to evaporate materials, depending on whether the materials are in wire, foil, ingot or powdered form. The material used as a resisitive source of heat is a refractory metal like W, Mo etc. One can evaporate from two or more sources in order to deposit a multilayer film of an alloy/compound. In this case, in addition to a thickness variation across the deposit there can be a composition variation also.

Direct thermal evaporation of intermetallic compounds may pose some practical difficulties. These compounds cannot be deposited without due consideration of their dissociation which may take place even below their melting points in some cases. There may arise difficulties in growing films of stoichiometric composition from alloys and complex chemical compounds. The adhesion of film to substrate depends on the level of purity of the substrate surfaces, procedure of its cleaning and film deposition condition., etc.

In order to overcome these difficulties, the technique known as flash evaporation may be used. It is generally used for deposition of materials whose constituents have vastly differening vapour pressures and which are known to decompose easily on vaporization. It is applicable to certain alloys, metal-dielectric mixtures and compounds. In most of the cases, vapours impinging on the substrate are highly supersaturated so that the film composition is not affected by condensation coefficients. In this technique, a fine powder of the compound is sprinkled over a heated sheet/boat, which is at a high temperature as compared to the melting point of the compound, to produce an instantaneous and complete evaporation of the compounds. Powder is kept in a feeder which is electromagnetically vibrated to let the powder drop slowly on the preheated boat.

2.2 ELECTRON BEAM EVAPORATION :

The temperature of the evaporant material can also be raised by electron bombardment instead of resistive heating. The thermionc electrons are accelerated through a potential of 5 KV to 10 KV and focussed on the material. The electrons loose their kinetic energy mostly as heat energy and the temperature at the focal point may be raised upto about 3000°C. At such a high temperature, most of the refractory metals and compounds can be evaporated. The temperature at the focussed point is very high, while rest of the material remains cool. The result is lesser interaction between the material and the support and reduced contamination. Evaporation rate can be varied by changing the input power.

2.3 MOLECULAR BEAM EPITAXY (MBE) :

The deposition of single crystalline (epitaxial) films by the condensation of one or more beams of atoms and/or molecules from Knudsen (effusion) source, under UHV conditions, is called molecular beam epitaxy.

Epitaxial films of compound semiconductors like GaAs, CdTe, etc. are usually deposited by this technique. The technique achieves precisely controlled properties of the film. The growth temperature is low, which minimizes the thermal effects like diffusion. The growth rate is also small (1 to 10 Å /sec.).

2.4 ACTIVATED REACTIVE EVAPORATION :

If the evaporated material (by resistive heating or electron beam evaporation) is transported through a reactive gas (oxygen, acetylene etc.) plasma, the deposition technique is known as activated reactive evaporation. It is used to deposit highly adherent films of oxides and carbides.

2.5 ION PLATING :

In this process the substrate and film are exposed to a flux of high energy ions during the deposition. The energy of the ion is high enough to cause the changes in the interfacial region and film properties such as adhesion of the film, its morphology and density. The evaporation of material is done by resistive heating or electron beam bombardment. A plasma is created in the working gas like argon either by keeping the substrate at high negative potential or by electrons emitted from a hot filament and accelerated to an anode. The negative potential at the substrate accelerates the ions to a desired energy(2).

III. EXPERIMENTAL SET UP FOR THIN FILM GROWTH :

3.1 Vacuum Coating System :

In the present work, the thin films were deposited by using "Hind Hivac" vacuum coating unit, Model NO. 12 A-4 (Figure-3). The chamber material is polished stainless steel with vacuum sealed glass 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 difussion pump OD-114 having oil charge of 150 to 200 cc. Rotary pump is connected with a moisture trap mounted directly above the inlet of the pump. A tray containing the dessicant in the form of pellets (usually activated alumina) 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 D.P. is connected with a 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 the D.P. to avoid the back streaming and increase the action of Diffusion pump.

The L.T. supply for filaments or boats is obtained from a 230V input transformer by means of series or parallel connections in the secondary of the transformer. The L.T. output of the transformer is fed through a current meter and a selector switch to L.T. leads and filament holders. It is also provided with H.T. power supply for glow discharge cleaning (ion bombardment), obtained from a high reactance transformer rated at 3.5 KV, 50 mA and 5 KV AC open circuit. A solid state power pack having DC output is provided for H.T. cleaning and cathode sputtering supply.

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 a Penning gauge fitted with the chamber and measuring from 10^{-2} torr to 10^{-6} torr.

3.2 Chamber arrangement :

The chamber gadgetary comprises of a work holder ring which has a useful diameter of about 8 inches. It is supported by three pillars fitted to the base plate. A D.C. high tension discharge cleaning system consisting of a pure aluminium annular ring suitably shielded to avoid electron contamination of the work. A source shutter swinging over the source position and operated by an external lever is provided on the front of the cabinet.

A standard filament holder is fitted to the L.T. live electrodes and an earth electrode. The filament is normally positioned vertically below the centre of the work holder to give nearly uniform distribution of the vapours. For deposition of a multilayered film, it is provided with a multifilament turret designed to evaporate four different materials without breaking the vacuum. The turret is rotated by external hand wheel.

Radiant heater : Radiant heater is fixed inside the chamber on the top of the work holder ring. This is capable of heating the substrate upto a temperature of 250°C within 30 minutes. The temperature measurement is made using a chromel-p-alumel thermocouple.

Electron gun : Electron gun is a vapour deposition source used to deposit thin films of a material whose melting point temperature is very high. It can achieve the temperature of about 3000°C. The material holder is water-cooled copper. The gun consists of three principal parts, a water cooled sample holder (Anode), a filament (Cathode) and a shield(3).

3.3 Thickness measurement :

Thickness is the most significant film parameter. It may be measured either by in-situ monitoring of the rate of deposition, 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. A 35° 20' quartz crystal cut called the AT cut, is generally used for the monitor because of its low temperature coefficient ($\pm 5 \times 10^{-6}$ between -20 and 60°C) for the resonant frequency. The frequencyof the fundamental resonance of a thickness mode for an AT cut crystal is given by (W.P. Mason)$^{(4)}$.

$$f = \frac{1}{2d}\left(\frac{C}{\bar{\rho}_q}\right)^{1/2} = \frac{N}{d} = \frac{1,670}{d} \text{ mmkc/sec} \qquad \ldots 1$$

$$N = (C/4\bar{\rho}_q)^{\frac{1}{2}} = 1,670 \text{ mmkc/sec.}$$

where d is the crystal thickness, $\bar{\rho}_q$ its density, C its shear elastic constant, and $N = (C/4\bar{\rho}_q)^{\frac{1}{2}} = 1,670$ mm/sec kc. Warner and Stockbridge$^{(5)}$ showed that a change in frequency Δf, due to a deposit of mass m, added to the area A of the antinodal surface of a mechancial resonator, is given by

$$\Delta f = \frac{-f\ km}{\bar{\rho}_q\ Ad} \qquad \ldots.2$$

where the const $K \simeq 1$ and the negative sign implies a decrease in the frequency. Combining eq. (1) and (2), we obtain.

$$f = \frac{-f^2\ km}{N\ \bar{\rho}_q A} = -Cf\ \frac{m}{A} = -C_f\ t\ \bar{\rho}\ \ _{film} \qquad \ldots.3$$

where $Cf = f^2 k/N\bar{\rho}_q$ is a constant of the crystal and $m = At\bar{\rho}_{film}$ assuming a uniform film of thickness t and a constant density $\bar{\rho}_{(film)}$. Thus $t = \Delta f/Cf\bar{\rho}_{film}$ yields average film thickness t and the constant density $\bar{\rho}_{(films)}$.

Δf is proportional to f^2, and so higher frequency crystals yield higher sensitivity.

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. As the deposition proceeds and the crystal starts receiving the coat, damping of oscillation takes place and hence the frequency change is observed. This change of frequency is related to the film thickness through the relation given above(4).

Rotary drive : The rotary drive is useful for uniform deposition of materials on large plane surface substrates. This consists of a work holder of 6 inches in diameter and is rotated by a variable speed electric motor situated outside the chamber, without vibrations. The speed is controlled by a solid state speed control.

X-ray diffraction analysis :

Among the various characterization techniques, X-Ray diffractometer plays a very important role in structural characterization. These techniques are used for a microstructural investigation of thin films and bulk crystals. By the Laue method using polychromatic X-rays, the crystallinity and symmetry of a crystal can be obtained in a qualitative way, by observing the nature and distribution of the Laue spots. The techniques based on the use of monochromatic radiation yield quantitave structural and symmetry properties possessed by the material being investigated.

In thin film work, the powder diffractometer is most commonly used. In diffroctometers, the diffracted radiation is usually detected by counter tubes which move through angular range of reflections. The intensities are recorded on synchronously advancing strip charts. An important feature of diffractometers is their ability to focus into a sharp diffraction line, the radiation which is Bragg reflected from an extended specimen area. This improves the sensitivity as well as signal to noise ratio.

There are two different designs of diffractometers used for thin film studies. The first one is "The Bragg - Brentano X-ray diffractometer". Here the specimen is mounted in the centre of the diffractometer and rotated by an angle Θ around the axis in the film plane. The counter is attached to an arm rotating around the specimen axis by angles twice as large as those of the specimen rotation. Only (hKl) planes parallel to the film plane contribute to the diffraction intensity.

The effective thickness of a film 't' decreases with the increasing diffraction angle. The intensity falls off rapidly for higher index reflections. The other design of diffractometers utilizes the Seeman Bohlin effect, in which the specimen and focussing circle remain stationary, while detector tube moves along the circumference of the focussing circle itself. It has an advantage that the angle of incidence is constant(6).

In the present study the X-ray diffractometer, Philips PM 8203 with pw 1390 channel control and pw 1373 goniometer have been used for the characterization of SnSe, $SnSe_2$, SnSe-$SnSe_2$ eutectic crystals and films. Laue back reflection patterns were obtained on X-ray machine supplied by Philips, Holland. Tungsten target was used at V=35 KV and A=20 mA with an exposure time of about 2 hrs.

Measurement of electrical resistivity and Hall coefficient :

The discovery of a great number of semiconductors among the intermetallic compounds has created urgent need for apparatus able to make fast accurate measurements of the resistivity and the Hall coefficient. Various sample geometries of films are in use for electrical and Hall measurements such as clove geometry and linear four probe geometry as described by Van der Pauw(7) and Goswami(8), respectively. For high value of resistances, linear four probe geometry is advisable. A sensitive current-meter and a stable power supply are connected in series with the sample. The volatge measurement is made by a sensitive and preferably a digital voltmeter. Change of resistivity with temperature is studied by keeping the sample inside a vacuum of the order of 10^{-5} torr in order to prevent oxidation. For heating the substrate, radiant heater is used. Temperature is sensed by a thermocouple which is kept in similar conditions with the substrate. Externally, the thermocouple is connected to a digital millivoltmeter to measure the thermo-EMF. For resistivity measurement on crystals, the Valde's four probe geometry is used. Here, the pointed tips of closely spaced probes are contacted on the sample surface. The method does not require the probes to be ohmic(9). This set-up is shown in Figure - 4.

FIGURE - 3 : Vacuum coating unit.

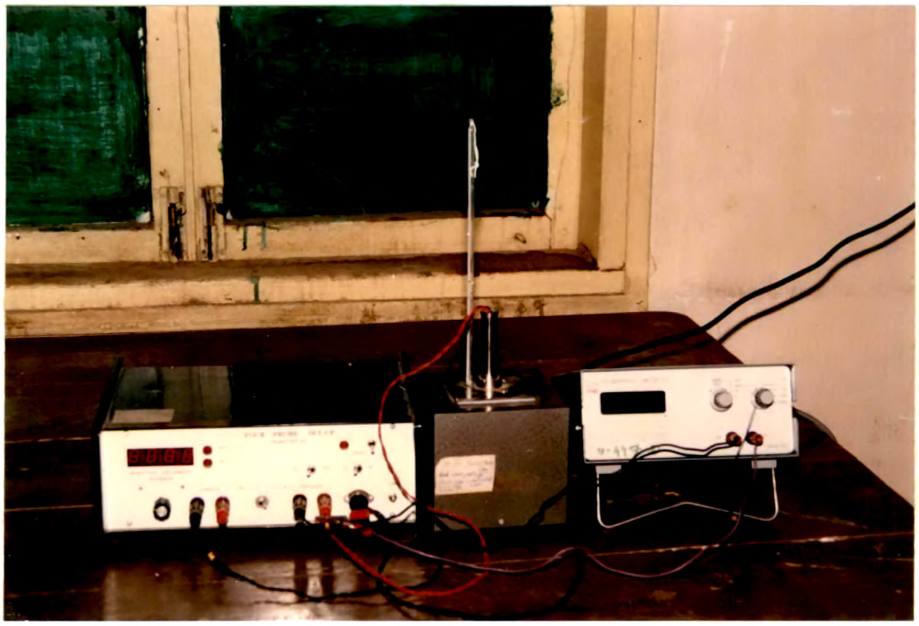

FIGURE - 4 : Valde's four probe resistivity set up.

For Hall measurement, linear five probe geometry is used. Charge carriers contributing the current caused by an applied electric field are deflected by a magnetic field applied perpendicular to the current. The resulting Hall voltage normal both to the current and the field can be measured. The sample is kept between the two poles of a strong electro magnet having magnetic field of the order of a few kilo gauss. A sensitive current meter is connected in series with a stabilised DC power supply and the sample . Across the other two contacts, digital microvoltmeter is connected. Current and voltage are measured in the absence and presence of the magnetic field. For both the measurements, the electrodes should be ohmic.

Measurement of Optical properties :

A dual beam spectrophotometer (Shimadzu, Japan UV-365) (Figure-5) is used for the study of the optical properties such as absorption, transmittance and reflectance of the samples, in the wavelength range of 2500 to 190 nm. From 2500 to 808 nm, it uses a PbS cell as the detector and changes to photomultiplier detector for wavelengths from 808 to 190 nm. For illumination in the range of 2500 to 303 nm, tungsten halogen lamp is used and below 303 nm, deuterium lamp is used. It is also provided with two monochromators (prism and grating) for better filtering(10).

Photoconductivity measurements :

Photoconductivity measurement is usually carried out in dark. For illuminating the sample a light source (like a Halogen lamp) is used. The sample geometry is either rectangular or circular. Finger shaped ohmic electrodes are deposited on the top of the film. The distance between the fingers is as small as possible. A digital voltmeter, picoammeter and a regulated D.C. power supply are used for the measurements. The picoammeter and regulated power supply are connected in series with the sample and the voltmeter is connected across it. A digital watch is used for the time measurement. Intensity of the light source is measured by a lux meter. The experimental set-up is shown in Figure - 6.

Photovoltaic measurements :

In the photovoltaic effect, we consider the junction with no external voltage. Two different layers of p type and n type semiconductors are deposited over an ohmic electrode. Above the top layer, usually finger geometry electrode is deposited.

The I-V characteristics are obtained using digital picoammeter and digital microvoltmeter in dark and under illumination. The intensity is measured by a lux meter. The C-V measurement is done by using an LCR bridge. Short circuit current, open circuit voltage, maximum power, fill factor and efficiency of the cell are obtained from these measurements.

The experimental schemes used in the present work are described in detail in the relevant chapters.

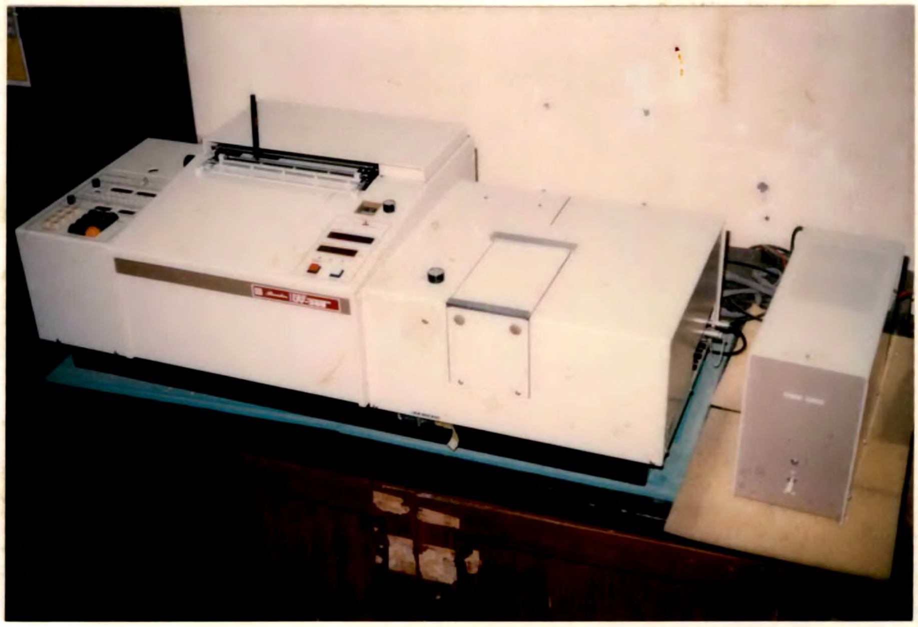

FIGURE - 5 : Spectrophotometer.

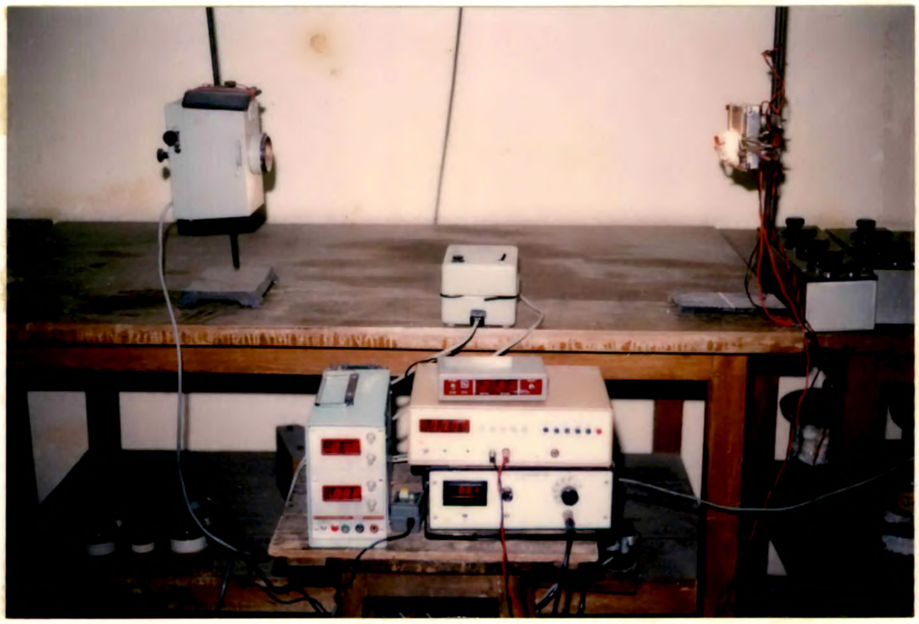

FIGURE - 6 : Photoconductivity measurement set up.

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