II

EXPERIMENTAL TECHNIQUES

CHAPTER-II

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2.1 INTRODUCTION

The substrates for thin film deposition are manufactured as shaped pieces with controlled tolerance from single crystals, glasses and ceramics.

The single crystalline substrates like MgO, $SrTiO_3$, YSZ, sapphire, silicon and germanium etc are obtained by cutting larger crystals (boules) into wafers. Most crystals are grown by the Czochralski technique, where a small crystal is dipped into the surface of the molten substrate material and slowly withdrawn.

Another method of crystal growth is flame fusion known as Verneuil technique, which was originally developed for the preparation of artificial gems. Large crystals of high purity and perfection have been grown by the Czochralski method which is more promising with regards to volume production. But every method requires slicing into wafers with subsequent grinding and polishing of the resulting surfaces.

Glasses are generally produced by mixing the raw materials at one end of a continuous tank-type furnace and with drawing the molten glass from the other end. For the glasses the softening point is the temperature at which a glass deforms under its own weight. Thickness of the glass can be controlled by adjusting the rate of draw.

For large are a applications the substrates in the thin film form are essential. In the present investigation we have tried to develop the deposition of SrTiO substrates in thin film form by electrolytic deposition tecnhique.

2.2 ELECTRODEPOSITION

Electrodeposition is a process of depositing a metal on the surface of another metal by passing D.C current through a solution containing metal ions to be deposited. By this process the coating formed on the metal surface changes the properties and dimensions of substrate metal.

The advantages of electrodeposition as a film forming technique include 1) The ability to form films on large and non planar surfaces such as wires, tapes etc. 2) The adaptability to large scale process 3) It is an isothermal process, mainly controlled by electrical parameters such as electrode voltage and current density, which are easily adjusted to control film thickness, morphology and composition 4) The freedom from carbon based impurities, it is not required to have very pure starting materials.

2.3 THEORETICAL BACKGROUND OF ELECTRODEPOSITION

Electrodeposition is governed by Faraday's two laws of electrolysis. The laws state that,

1) The amounts of substances liberated at the electrodes of a cell are directly proportional to the quantity of electricity which passes through the solution.

2) The amounts of different substances which are deposited, or liberated, by the same quantity of electricity are proportional to their chemical equivalents weights.

These laws further predict that,

i) Measuring the quantity of electricity that passes one can measure the amount of chemical change produced.
ii) Knowing the chemical equivalent weight of the substances that will be liberated is calculated by a given quantity of electricity.

Some Terms Used In Electro-synthesis

Electrolytic Cell : A cell consists of two electrodes and one or more solutions in an appropriate container. If the electrical energy is supplied from an external source the cell through which it flows is termed as electrolytic cell and Faraday's laws account for the material changes at the electrodes.

Cathode : The cathode is the electrode at which reduction occurs. In an electrolytic cell it is the electrode attached to the negative terminal of the source, since electrons leave the source and enter the electrolysis cell at that terminal.

Anode : The anode is the electrode at which oxidation occurs. It is the positive terminal of an eletrolysis cell.

Current Density : The current density is defined as the current per unit area of electrode surface. It is generally expressed in amperes per square meter A/m^2 or mA/cm^2 of the electrode surface.

Current Efficiency : By measuring the amount of a particular substance that is deposited and comparing this with the theoretical quantity (calculated by Faraday's Laws), the actual current efficiency may be obtained. In general, analytical deposition show low current efficiencies owing to other reactions which occur during the electrolysis, for example, liberation of hydrogen during the later stages of the deposition of a metal at a cathode.

Electrode Potential : When a metal is immersed in a solution containing its own ions, a certain potential difference is developed between the metal and the solution and is called the electrode potential. The potential difference E for an electrode reaction

$$M^{n+} + ne \rightleftharpoons M$$

is given by the expression

$$E = E^{o} + \frac{RT}{nF} \ln a_{M^{n+}} \qquad \text{---------------} \quad (I)$$

Where,

E^{o}- is a constant characteristic of the metal

R - is the gas constant = 8.3143 $J.K^{-1}$ $mole^{-1}$

T - is the absolute temperature in Kelvins

F - is the Faraday's constant = 96500 Coulombs

n - is the valency change and

a - is the activity (concentration) of the ions.

For most purposes in quantitative analysis it is sufficiently accurate to replace a_{M^+} by C_{M^+}, the ion concentration (in moles/dm^3).

If in equation (I) a_{M+} is put equal to unity, E^o is called the standard electrode potential of the metal.

In order to determine the potential difference between an eletrode and a solution, it is necessary to have another electrode and solution of accurately known potential difference. The two electrodes can then be combined to form a voltaic cell, the e.m.f of whih can be directly measured. The electromotive force of the cell is arithmetical sum or differene of the electrode potential. The value of the unknown potential can then be calculated. The primary reference electrode is the normal or standard hydrogen electrode.

<u>Electrolysis</u> <u>And</u> <u>Polarization</u> : Before electrolysis starts in a solution, potential of two electrodes are alike, but as electrolysis proceeds, it will be observed that the potential of the anode becomes more positive, that of the cathode negative than the initial or equilibrium potential. The change in the potential of the electrode as a result of electrolysis is called the polarization of the electrode. In a state of equilibrium for reversible electrode the discharge of ions and their reformation, take place at the same time and there is no net current flow. If the conditions are such that there is actual passage of current, the

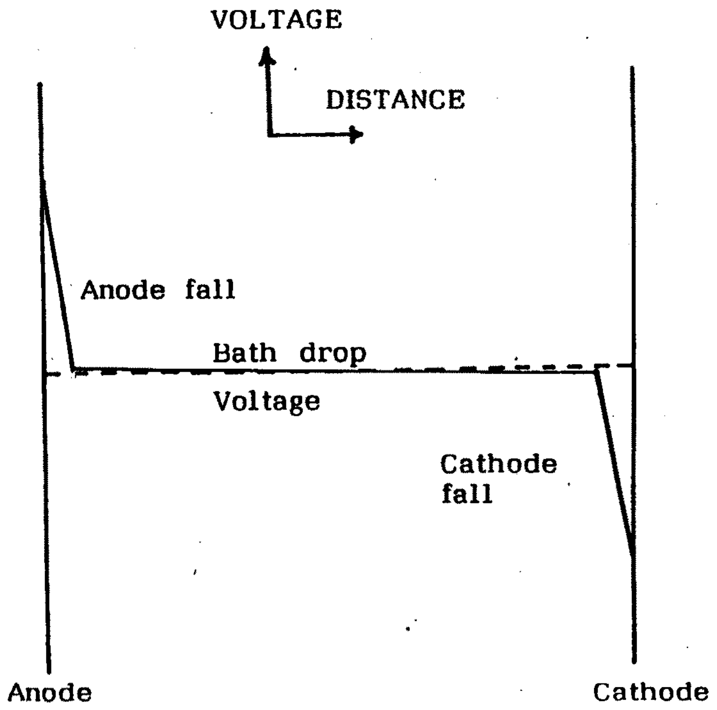
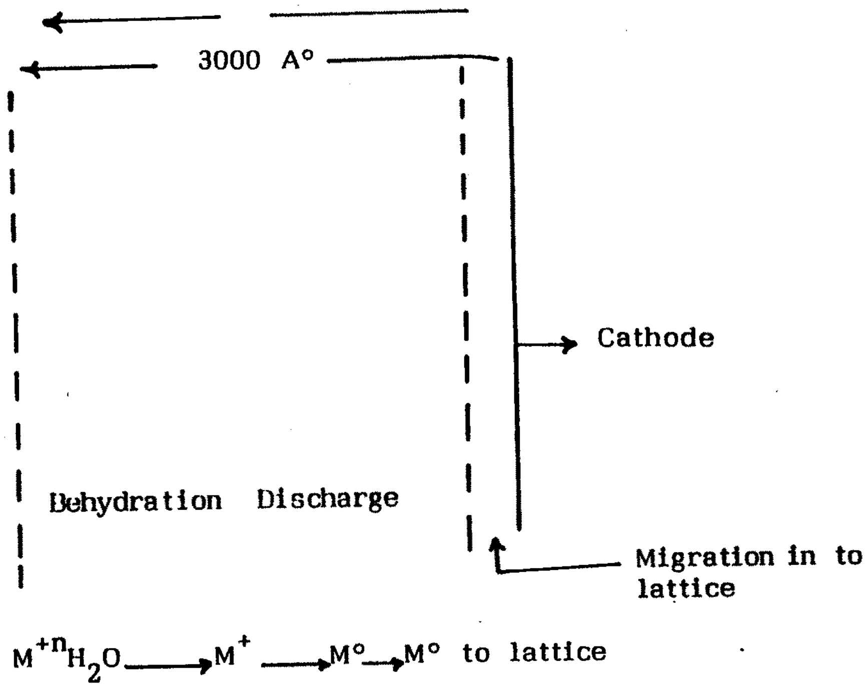


Fig.1 Mechanism of electrodeposition



electrode is disturbed from its equilibrium condition. This disturbance of equilibrium state associated with the flow of current is called eletrolytic polarization and the disturbed electrode is said to be polarized(Fig.1).

2.4 EXPERIMENTAL SETUP FOR ELECTROLYTIC DEPOSITION

1) Scanning potentiostat
2) Electrolytic cell
3) SCE
4) X-Y recorder.

1) Scanning Potentiostat :

Scanning potentiostat is concerned with the study of voltage current time relationship during electrolysis is carried out in a electrolytic cell. The technique commonly involves studing the influence of voltage changes on the current flowing in the cell.

In the present investigation we have used potentiostat/galvanostat model 362(EG & G) and X-Y recorder.

2) Electrolytic Cell :

Electrolytic cell consists of three electrodes (3). The negative terminal of D.C source is connected to the object (the cathode) the working

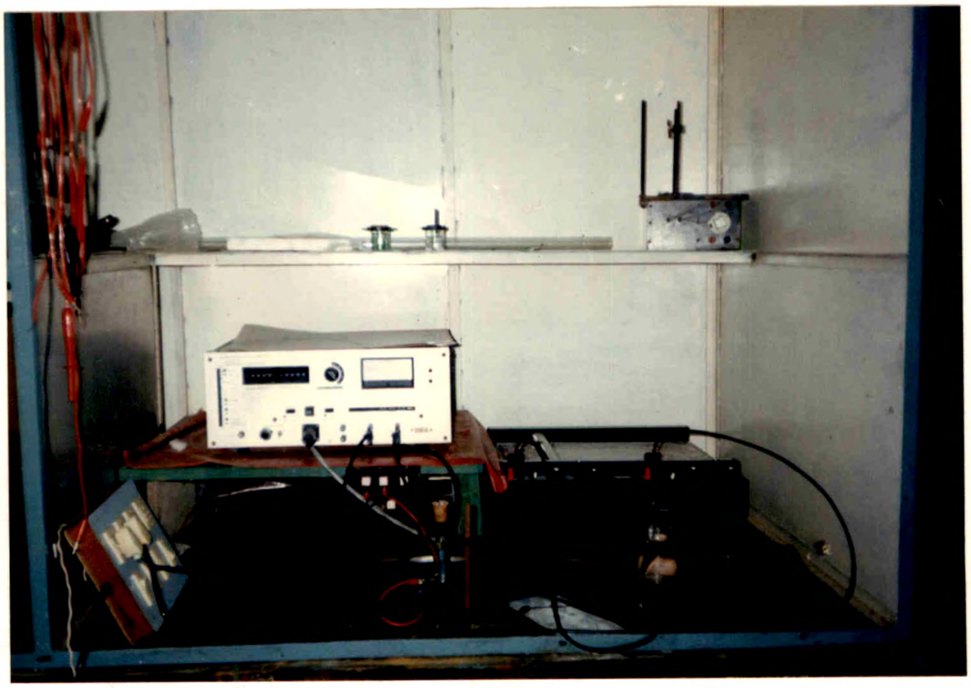


Fig. : Photograph of Experimental Set-up for Electrodeposition
1) Scanning Potentiostat
2) X-Y Recorder
3) Electrolytic Cell

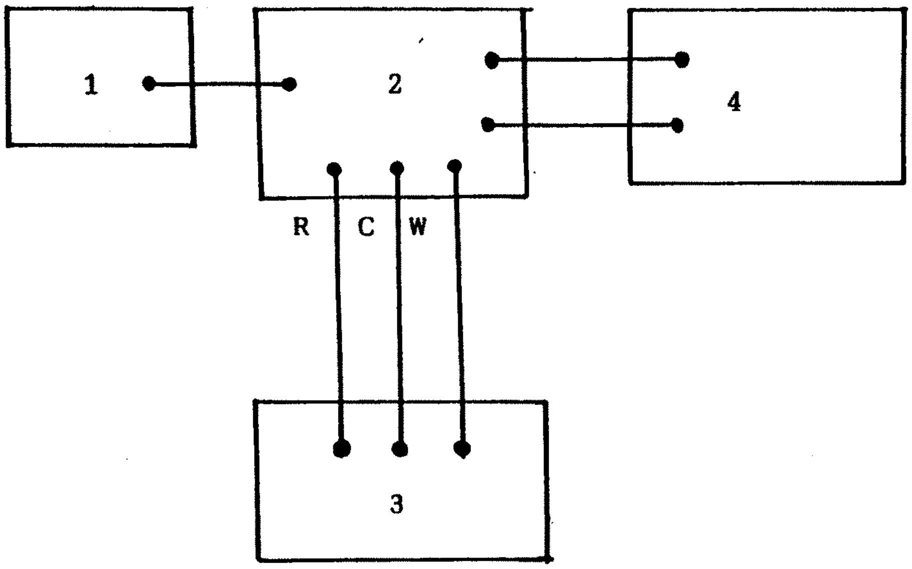
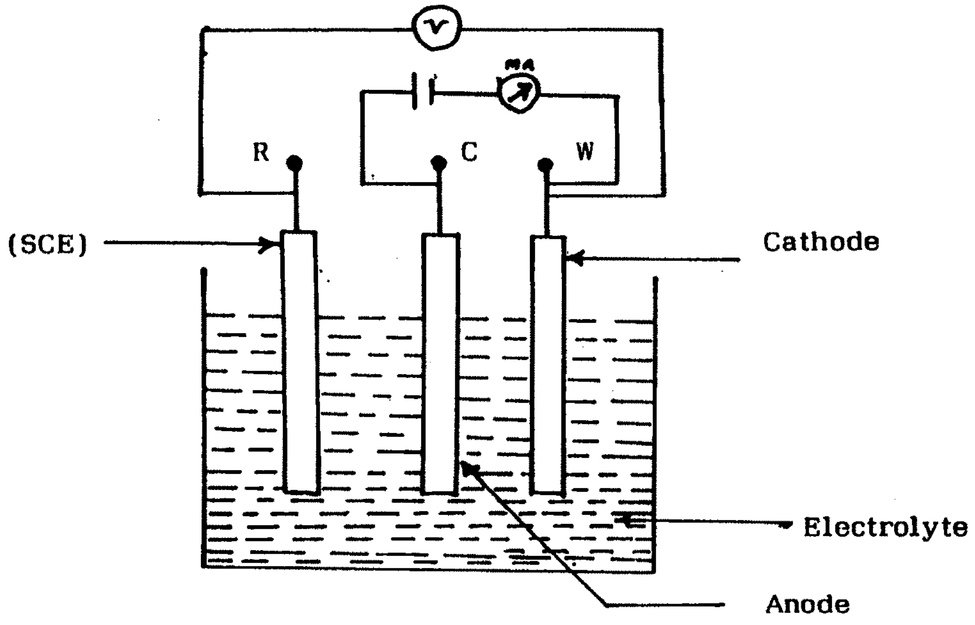


Fig. 2 <u>Experimental set up for electrodeposition</u>

1 Power supply
2 Potentiostat
3 Electrolytic cell

R Reference electrode (SCE)
C Counter electrode (Anode)
W Working electrode (Cathode)
4 X-Y recorder



electrode(W) while the positive terminal is connected to the counter electrode (C) and the reference (R) terminal is connected to the saturated calomel electrode (SCE) to measure the potentials of cathode with respect to it.

In the present work we have used 50c.c volume glass cell. The cell dimensions are 1.5 cm in radius and 3 cm in height. The cathode areas were kept parallel to the anode area. The cathode was 40mm x 10mm x 0.5mm in rectangular shape. Anode was a pure graphite plate of 40mm x 15mm x 2.5mm in dimension. The parallel distance between cathode and anode was kept 5mm (Fig.2).

3) SCE :

Saturated calomel electrode is a reference electrode used to measure the standard electrode potential of metal electrodes (a metal in contact with a solution of its ions of unit activity). Due to its ease of preparation and constancy of potential instead of standard hydrogen electrode. SCE is used more frequently.

In this calomel electrode mercury and calomel (mercury chloride) are covered with potassium chloride solution of definite concentration. The potassium chloride solution must be saturated with the calomel. The electrical contacts are made with platinum wire dipped into the mercury. The potentials of the 0.1N, 1.0N and saturated calomel electordes at 25°C relative to the normal hydrogen electrode are 0.3371, 0.2846 and 0.2458 volts respectively.

4) X-Y Recorder :

In the present investigation we have used X-Y recorder with potentiostat/Galvanostat model 362(EG&G). The applied voltage can be varied at a steady rate in the range 20mV/sec to 100mV/sec and simultaneously change in current can be recorded with X-Y plotter. The curves obtained with this instrument are graphical representation of the polarization of electrode and are called polarograms.

2.5 RECORDING OF VOLTAMOGRAM

Voltamograms are recorded by drawing the current voltage curves. These are plotted with applied emf (voltage) as abscissae reading in increasing negative values on the right; current is plotted as ordinates, cathodic currents (resulting from reduction) being regarded as positive and anodic currents negative. The height of the curve (wave height) is the diffusion current, and is a function of the concentration of the reacting material. The potential corresponding to the point of inflection of the curve (Fig. 3) is characteristic of the nature of the reacting material.

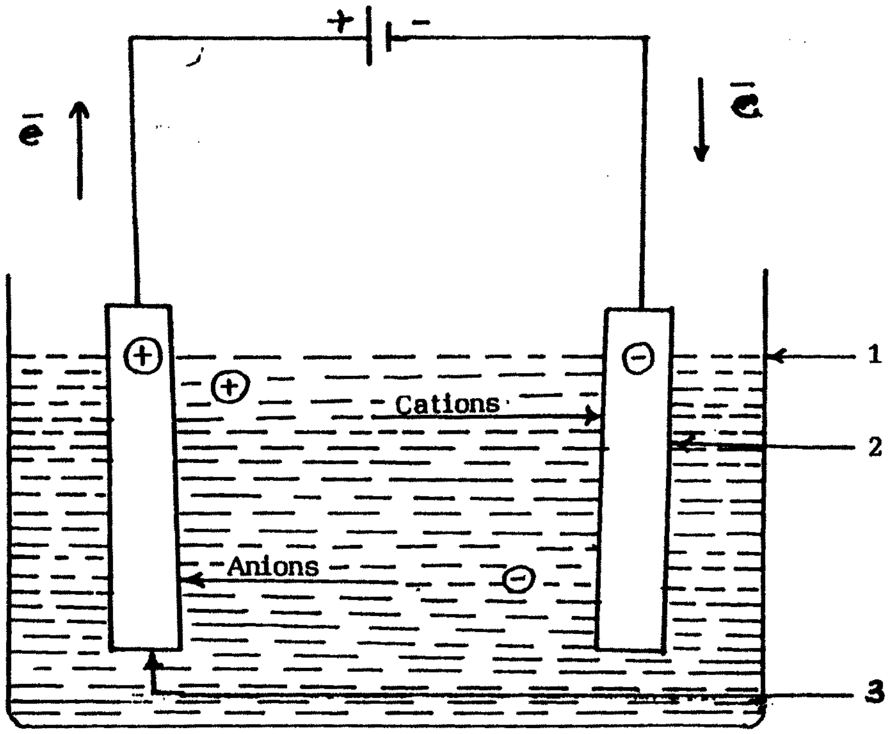


Fig.2 A schematic representation for the mechanism of electrodeposition

1) Plating bath

2) Cathode

3) Anode

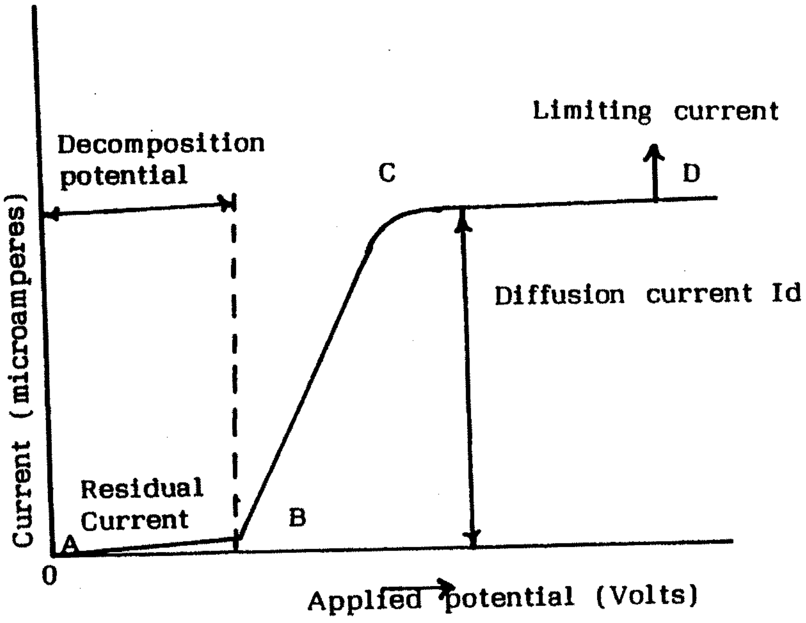


Fig. 3 : Voltamogram (polarogram)

When an external e.m.f is applied to the electrolytic cell, charged with a dilute solution of the material under examination, all the positively charged ions present in the solution will be attracted to the negative working electrode by; (a) an electric force, due to the attraction of oppositely charged bodies to each other, and by (b) a diffusive force, arising from the concentration gradient produced at the cathode surface. The total current passing through the cell can be ragarded as the sum of these two factors. A typical simple current-voltage curve, the voltamogram is shown in figure (3).

The working electrode, being perfectly polarizable, assumes the correspondingly increasing negative potential applied to it. From A to B practically no current will pass through the cell, At B, where the potential of the electrode is equal to the deposition potential of the material ions under examination, with respect to reference electrode, the current suddenly commences to increase and the working electrode becomes depolarized by the metallic ions, which are then discharged upon the electrode surface to form metallic element, consequently a rapid increase in the current flowing through the cell will be observed. At the point C the current no longer increases linearly with the applied potential but approaches a steady limiting value at the point D. At any point on the curve between B and C the number of metallic ions reaching the electrode surface as a result of migration and diffusion from the solution eceeds the number of metallic ions from the solution to the cathode surface become equal to the rate of deposition. At potentials more negative than point D, the concentration of the undischarged metallic ions at the working electrode surface is negligibly small relative to the metallic ion concentration in the bulk of the solution. Therefore, no further increase in current passing through the electrolyte is expected for more negative voltages.

2.6 OXIDATION SYSTEM

Through oxidation process metallic, binary and ternary alloyed films can be converted to oxide films. Thin film properties are changed after deposition by oxidation or annealing processes. The electrical properties of thin films are sometimes stabilized by heating after deposition. At higher temperature recrystallization processes are enhanced, which occur very slowly at room temperature.

Oxidation system comprises of

a) Furnace
b) Oxygen cylinder
c) Temperature controller and
d) Supplies.

In the oxidation system furnace is set at required particular temperature with temperature controller and power supply. Thin film samples which are to be oxidised are kept in a continuous flow of oxygen from the inlet of furnace, with outlet of the furnace dipped into the distilled water contained, taking precaution that water does not enters the furnace. The samples can be oxidised for a fixed time period and quenched or can be cooled at room temperature with temperature time controler.

2.7 XRD (X-RAY DIFFRACTION)

In the present work we used Philips, PW-1710 X-ray diffractometer, using CuK_α radiations with wavelength λ = 1.5405 A°. The x-ray machine was operated at 40KV and 30mA. The specimen sample for diffractrometric work were prepared by electrodeposition of Sr-Ti and $SrTiO_3$ allys on a stainless steel plate of size 3.5cm x 2.0cm.

The specimen sample prepared was placed on the sample holder of the diffractometer. The range of scanning angle 2θ was selected. The memory plots were obtained. These memory plots depict the peak number observed d values and counts per half second which are proportional to diffracted intensity.

2.8 RESISTIVITY MEASUREMENTS

Resistance measurements of the electrodeposited samples are done with usual two probe technique. An air drying silver past used to make electrical contacts on the sample. A eight and half digital HIL 2665 multimeter was used. Electrodeposited specimen of 1 x 1 cm were given silver paste contacts. Resistance measurements were obtained for deposited and oxidised samples at varied temperatures and time.

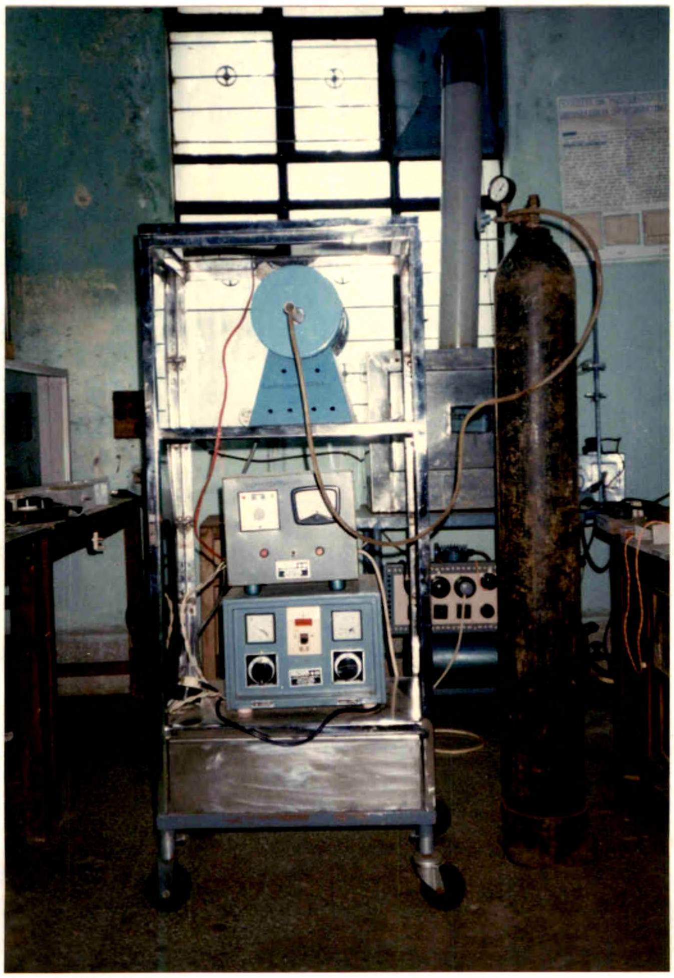


Fig. : Photograph of Oxidation System

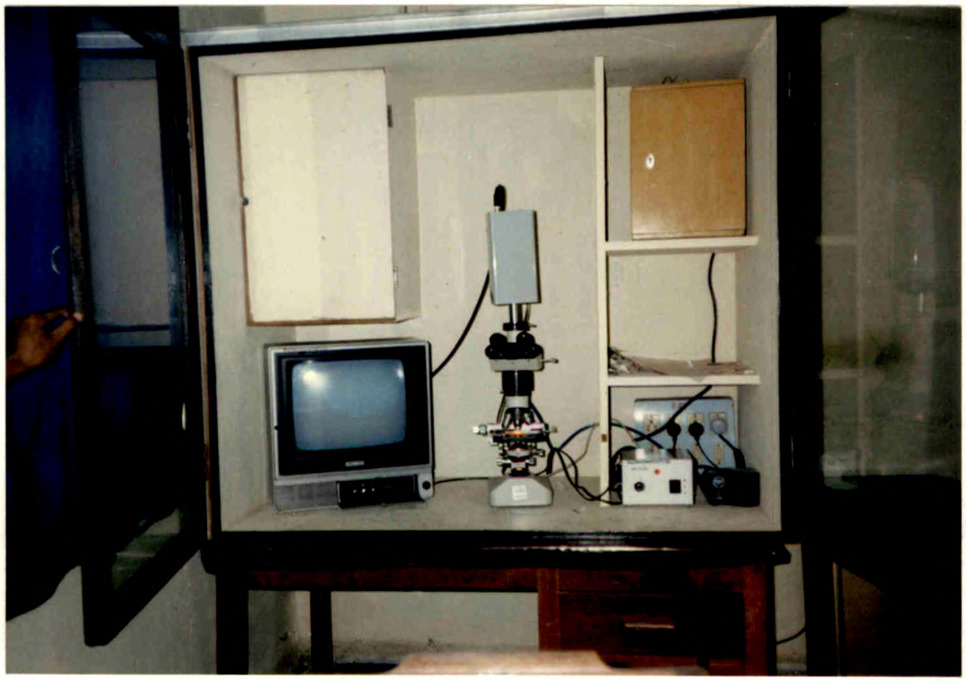


Fig. : Photograph of Optical Microscopy System

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