CHAPTER-III

C H A P T E R - III

DESIGN, FABRICATION, AND EXPERIMENTAL TECHNIQUES. 80

3.1 Introduction.

The essential theoretical aspects and details of processes involved in both the thin films and the photoelectrochemical cells are outlined in chapter - II. As the moto of our work is to prepare an efficient material for the conversion of optical energy into an electrical, it is highly essential to characterise the photoelectrode material in terms of its film properties and cell properties when it is used as a sensitive electrode in a photoelectrochemical cell. This chapter is fully devoted to the design and fabrication aspects and experimental techniques involved in preparing and characterizing the photoelectrodic material and its use in a PEC cell. The section 3.2 gives details of the fabrications and developments of a chemical deposition system. The procedure and technical know how for the deposition of Bi_2S_3 thin films is presented in section 3.3. The section 3.4 describes the techniques for electrical (via conductivity and thermoelectric power) and optical (via optical absorbance and band gap) characterisations and the design, and fabrications involved therein. The section 3.5 points out the essentials of fabrication of a PEC cell and an experimental arrangements for the electrical and optical properties of a PEC cell.

3.2 Development of a Chemical Deposition System.

As a pioneer worker of this laboratory,a gradual

development of a chemical deposition process was undertaken in view to optimise the different parameters and mechanical adjustments. The photograph of the minimum requirements of the experimental set up necessary for the deposition of Bi_2S_3 films is shown in fig.3.1.Essentilly it consists of a dust proof chamber,an oil trough and constant temperature assembly, reaction vessel and substrate holder.

3.2.1 Dust proof chamber :

A metallic dust proof, clean chamber of the dimensions 1.8 x 0.8 x 1 meter was designed and fabricated in order to avoid contamination of the samples by dust particles, humidity, natural gases etc. An outlet at the top of the chamber is fitted to a exhaust fan via a hollow pipe to remove the gases evolved during the film deposition.

3.2.2 An oil trough and constant temperature assembly:

A leak proof stainless steel oil trough of the dimensions 21 x 16 x 10 inch with 27 litre in capacity, supplied by Modern Industrial Corporation, Bombay, was used in order to achieve the required temperature. In order to minimise thermal losses from the trough, a glass wool was interposed between the inner stainless steel and outer metallic walls. A 2000 W electric heater was used to heat the paraffin oil within an accuracy of $\pm 0.5^{o}C$. A synchronous universal motor was used for continuous churning of the oil to maintain the constant and uniform temperature throughout

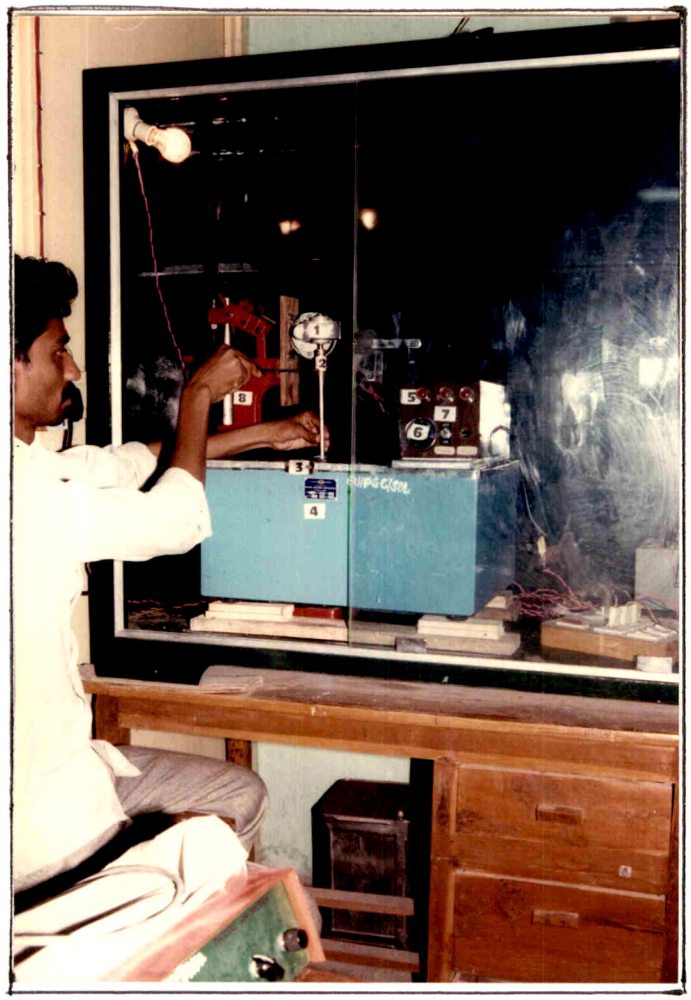

Fig.3.1. Photograph showing the essentials of a Chemical deposition system;
1) Constant speed AC gear motor, 2) Substrate holder,
3) Reaction container, 4) Paraffin Oil trough,
5) Electric heater, 6) Temperature controlling assembly with sensor, 7) Oil stirring motor, and
8) Drilling machine stand.

the oil trough.

3.2.3 Reaction Vessel :

It was a 250 ml Borosil glass beaker to which appropriate amounts of solutions of bismuth nitrate, ammonia, and thiourea were mixed. The mixture was heated to a suitable temperature using an oil trough. The required amount of solutions were taken in a beaker and the assembly was fixed to an oil trough as shown in the fig. 3.2.

3.2.4 Substrate holder :

The chemically deposited Bi_2S_3 films in respect of their quality are dependent on the geometry of the substrate holder. Hence a substrate holder as shown in fig. 3.3 was designed and fabricated in our laboratory. It consists of a circular bakelite disc of 5 cm. in diameter and 1.2 cm. thick. The disc was slotted to fix the substrates in such a way that each slot is exactly perpendicular to the other (i.e. the slots were cut into the holder making 30°, 120°, 210° and 300° angles with respective diameters of the holder). As every substrate is perpendicular to the other, a proper but continuous bulk churning of the solution in reaction vessel, in all possible directions, was made possible. The stem of the substrate holder can be fitted to a universal constant speed A.C. gear motor via a bushing arrangement fabricated in our laboratory. The motor was permanently fitted to a drilling machine stand. The drilling machine stand was

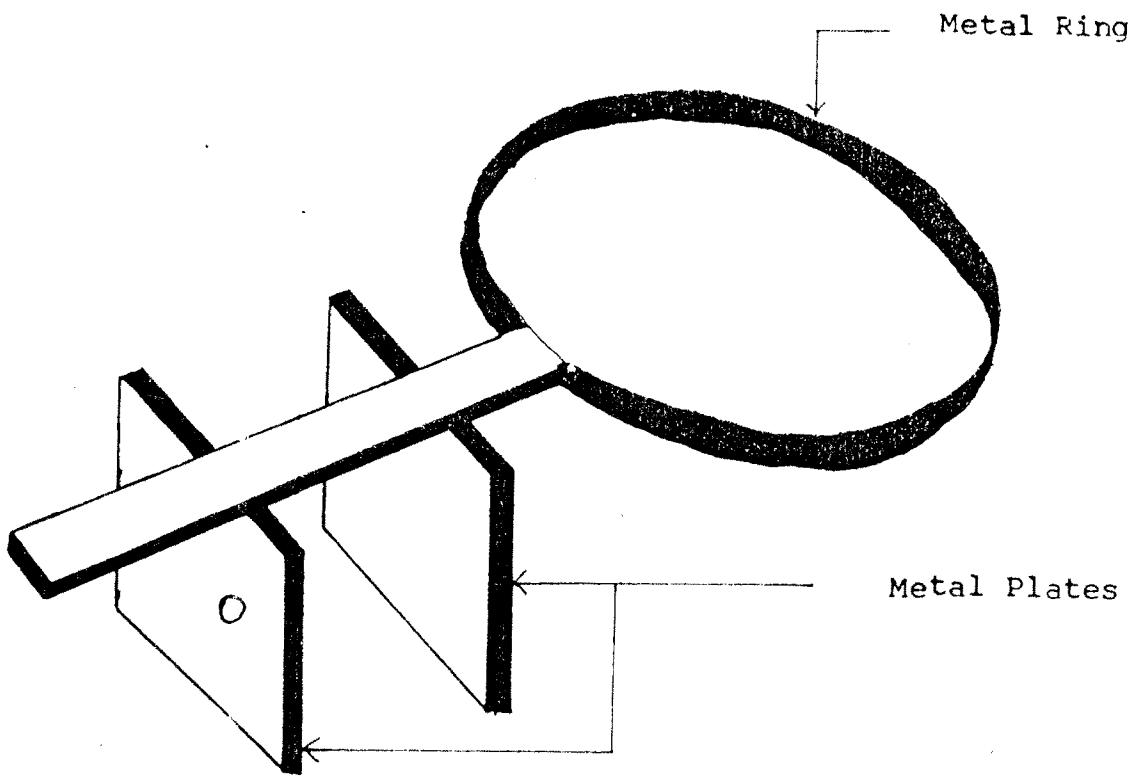

Fig.3.2 Reaction vessel stand.

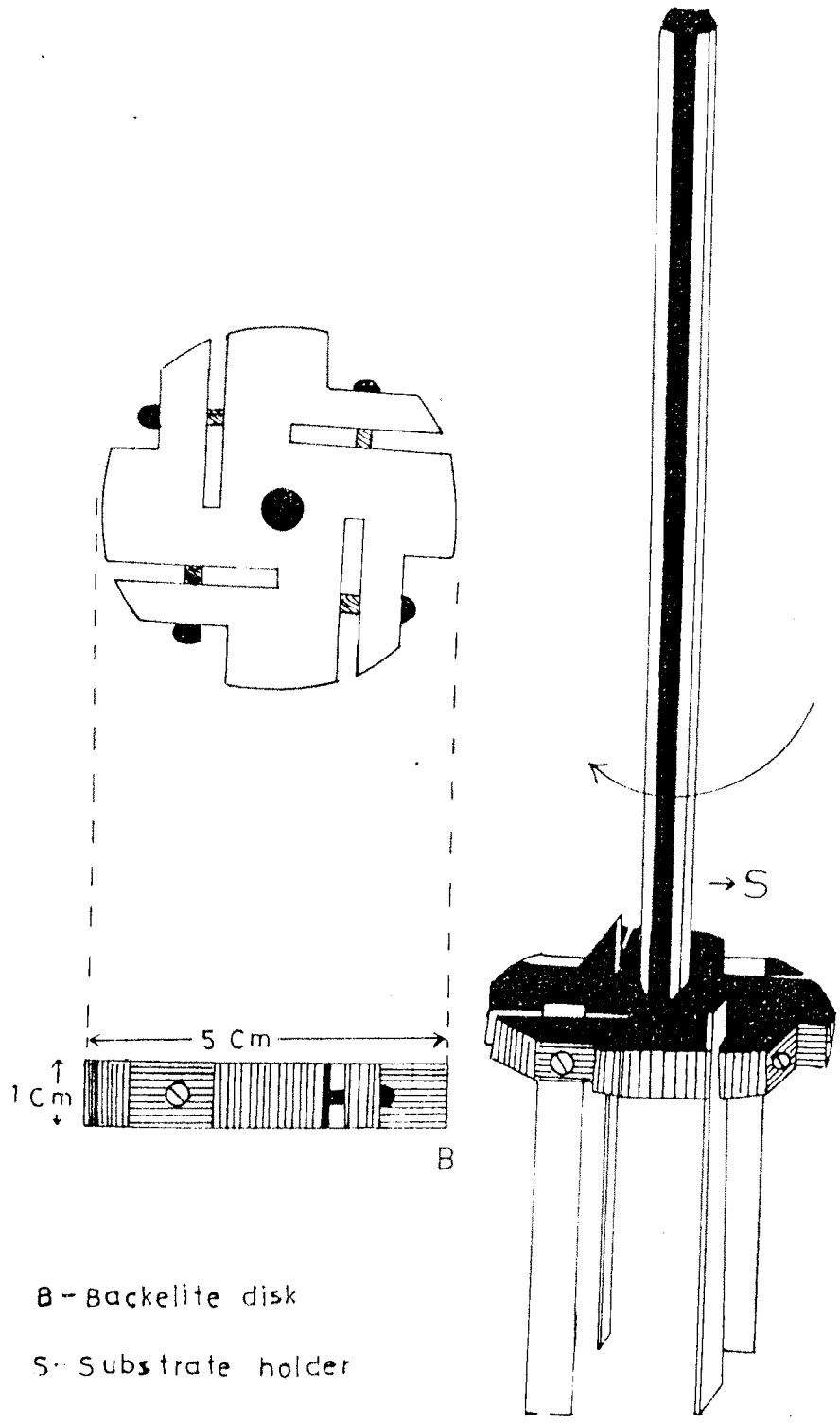

Fig-3·3 Design of the substrate holder

modified in such a fashion that we can adjust any constant position of the motor. For the experimental purpose we adjusted the position of the motor so as to dip more than 2/3 portion of the substrates into the reaction vessel. The care was taken from touching any of the substrates to the walls of the reaction container which may cause serious damages or scratches to the samples and breaking of the reaction container.

3.3 Deposition of Bi_2S_3 Thin Films :

There are so many methods in existence for the preparation of thin films. The choice of a particular method has a direct bearing on various factors like material to be deposited, nature of the substrates, required film thickness, structure and quality of the films, application of the films etc. Among the most widely used methods for the deposition of Bi_2S_3 thin films such as vacuum evaporation, sintering, sputtering, spray pyrolysis, chemical deposition process, the later is relatively less expensive, simple and provides a convenient means in which a variety of substrates like metal semiconductor and insulator can be used |16,25,26|. Film deposition by this method is a slow process which allows for better stoichiometry and crystallinity |40,42,16| compared to other methods. Impurity doping can easily be achieved by addition of a proper volume of the required concentration of a desired dopant directly into the solution container |40|.

3.3.1. Preparation of the substrates :

The substrates used in the various stages of this work were amorphous glasses (microslides) and good quality stainless steel. Especially, stainless steel substrates were used while studying photoelectrochemical properties. Film properties were studied on amorphous glass substrates.

a) Preparation of the glass substrates :

The amorphous glass substrates of approximately 100% transmission were procurred from Blue Star, Bombay (size 72 x 25 x 1mm.). These are cut finely by means of a diamond point into the substrates of the size 72 mm x 9mm x 1 mm and were utilised for the deposition and further studies.

b) Preparation of stainless steel substrates:

A stainless steel sheat of suitable guage (24) was cut into the strips of the size 75 x 9 x 1mm and were used as a substrate. The substrates were polished to a mirror grade by using an emery cloth and a polishing paper (0-paper). The above good polished stainless steel strips were employed for the deposition.

3.3.2. Substrate cleaning :

The key precaution taken before the deposition of Bi_2S_3 films is the careful cleaning of the substrates procurred as above. As the stickness of the film layer has a direct bearing on cleanliness of the substrate, following was the procedure adopted while cleaning the substrates. The glass

substrates were boiled in chromic acid for about 20 minutes and washed with double distilled water. They were further dipped in a medium concentrated teepol detergent solution and washed several times with double distilled water and then with ultrasonic cleaner. All the substrates were kept immersed in double distilled water before use. In the similar fashion, stainless steel strips were first degreased by washing with mild teepol solution and then polished (mirror smooth) on a sylvate emery cloth. Further procedure was similar to glass substrates except the use of chromic acid.

3.3.3. Preparation of the solutions :

All the basic ingradients used for the preparation of Bi_2S_3 thin films, were brought into their ionic form by using a fresh double distilled water. Following were the chemicals used : i G.R. grade bismuth nitrate supplied by B.D.H. (India). ii A.R. grade thiourea supplied by Loba Chemie. (Bombay) India. iii G.R. grade Triethanolamine, Loba chemie (Bombay) India. iv L.R.grade ammonia supplied by B.D.H. Glaxo Laboratories (India).

3.3.4. Deposition of Bi_2S_3 films :

Thin layers of Bi_2S_3 were prepared in an alkaline medium by a modified chemical deposition process [39,41,42] by allowing to react triethanolamine complex of Bi with S ions, which are released slowly by dissociation of thiourea

[16,40,42,44]. The substrates used were non conducting glass microslides and stainless steel strips of the size mentioned earlier. The detailed procedure is as follows: A 20 ml. of the 0.01 M freshly prepared solution of Bi ions, obtained by triturating G.R. grade bismuth nitrate in a sufficient quantity of triethanolamine, was taken in a glass beaker 250ml in capacity. A freshly prpared 30 ml. 1 M thiourea solution and 5 ml. 14 N, aqueous ammonia were added to it. The total volume of the reaction mixture was made upto 200ml. The pH of the solution was adjusted around 9.5. The temperature of the reaction mixture was raised to 95 $\pm$ 0.5^{o}C. The glass substrates of the dimensions 72 x 9 x 2 mm. were thoroughly cleaned and kept immersed (more than 2/3) in the reaction mixture by means of a specially designed substrate holder. The substrate holder was attached to a constant speed gear motor. The reaction mixture was fitted to an oil trough by means of an iron 'O ' ring fabricated in our laboratory. The temperature of an oil trough was controlled within 2^{o}C. The substrates were rotated at a speed of 70 r.p.m. in the reaction mixture for about 40 minutes. After 40 minutes the samples were taken out, washed several times with distilled water, dried in air and left in a dark desiccator.

3.4 Characterisation of The Films :

As our main intention is to obtain an acceptable output

power from a PEC cell, it is highly essential to characterise the photoelectrode material in thin film form. The experimental details of few of the properties of the thin samples are described in this section.

3.4.1 Measurement of thickness :

The thickness measurement was carried out by a weight difference method in which mass, area and density of the material was considered. The film thickness is related to the mass, area and density of the material as ;

$$t = \frac{m}{A.d.} \qquad \ldots 3.1.$$

where , m = weight in grams of the sample.

A = area in cm^2 of the sample.

d = density of the material (6.78gm/cm for Bi_2S_3)

3.4.2 Microscopic and XRD studis :

The microstructure of the samples was observed with an optical microscope Leitz Laborlux, 12 POL W.Germany.

The XRD studies on a powdered samples were examined within a span of angles between 20^o to 80^o by a phillips PW - 1710 X-ray diffractometer with CuK lines.

3.4.3 Design, fabrication of conductivity measuring unit and measurement of conductivity :

The dark conductivity of the samples was measured by using a conductivity measuring unit as shown in fig.3.4 designed in our laboratory [39]. It consists of two brass

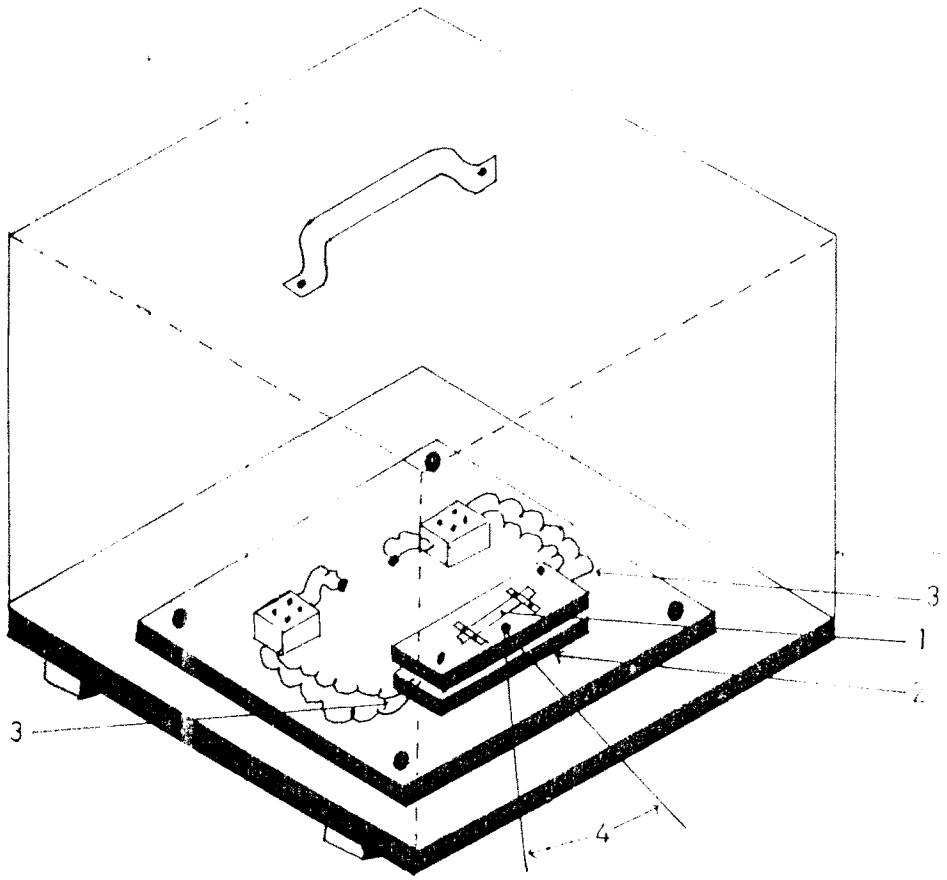

Fig.3.4 Design and experimental arrangement for the measurement of conductivity.
1) Sample , 2) Brass plates,
3) Electrical heaters, 4) Thermocouple,
5) Shield.

plates of the size 10 x 5 x 0.6 cm. One of the plate is fixed tightly on a asbestoss base of the dimension 10 x 10 inches. Two strip heaters (65 watt) were kept in parallel on the first brass plate and other plate was fixed tightly to the lower plate. i.e. strip heaters were sandwiched in between the two brass plates to achieve the uniform temperature. A mica sheet was used to wrap the heaters before being put in between the brass plates so as to achieve the electrical insulation for either of the brass plates. A sample holder of the dimension 3 x 0.5 x 0.6 cm. was designed and fixed permanently exactiy at the centre of the upper piate.A sample whose conductivity was to be measured was mounted with a copper press contacts below the sample holder. The sample was electrically insulated from upper brass plate and the sample holder by interposing the mica pieces at the proper places.Thermal radiation losses were reduced by covering the whole set up in a bakelite box. The box was coated inside by the asbestoss sheets. The working temperature was recorded with a Chromel Alumel thermocouple (24 guage) fitted at the centre on the top of the upper plate. The Aplab TPSU (transistorised power supply unit) was used to pass the current through the sample. The potential drop across the sample was measured with the help of digital multimeter (pla-DM-14B) and current through the sample was noted with a sensitive HIL - 2665, $4\frac{1}{2}$ digits nanoammeter.

3.4.4 Design, fabrication of thermoelectric power (TEP) unit and measurement of TEP :

The necessary conditions and requirements for thermoelectric power measurement such as maximum temperature difference and minimum contact resistance have been discussed by Bauerie et.al. |89| . The necessary care was taken to fulfil the above requirements while fabricating the thermoelectric power unit. Fig. 3.5 shows a schematic of the TEP measurement unit. It consists of two copper plates of the dimension 5 x 4 x 1.2 cm. fitted on a asbestos sheet supported by a bakelite sheet. The plates were arranged in parallel separated by a distance of 0.5 cm. The plates were pitched to a size of the miniheaters,from the bottom and the miniheaters of the different wattage (65 W and 35W) were fixed in them. Care was taken of the electrical insulation between the miniheaters and the copper plates by means of a mica sheet. A pair of sample holder was fabricated in our laboratory in a similar fashion as that of the conductivity measurement and fixed on the top adjuscent nearer edges of the copper block lengthwise. The sample size used in this study was 2.5 x 0.5 cm. on amorphous glass substrate and the dimensions of the substrate holder were 3 x 0.5 x 0.5 cms. The sample was electrically insulated from copper blocks and the substrate holder by means of a mica pieces. The press copper contacts were used for the measurement. Chromel-Alumal

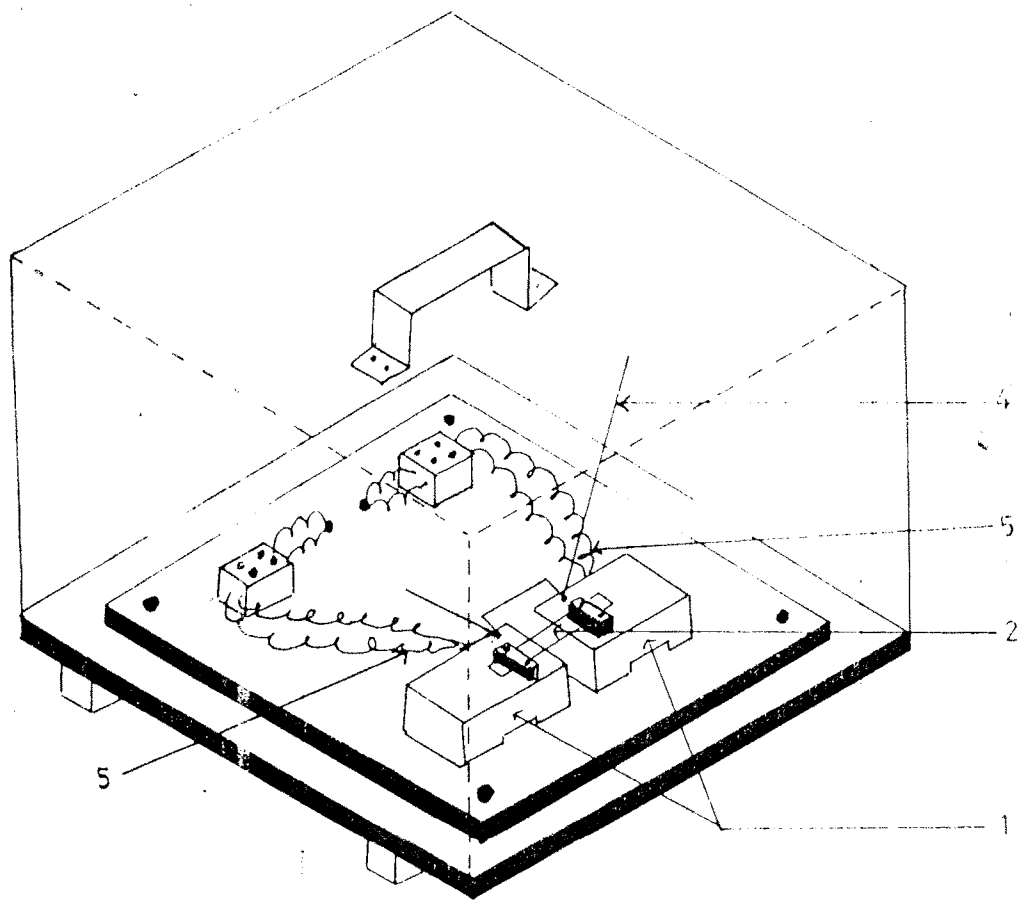

Fig.3.5 Design and experimental arrangement for the measurement of TEP:
1) Copper blocks, 2) Sample,
3) Thermocouple(mean temperature recorder),
4) Differential thermocouple (thermovoltage recorder),
5)Heaters.

thermocouples (24 guage) were fixed on the top of the copper blocks for the temperature. The proper shielding of a unit was made by a bakelite box to minimize the losses due to thermal radiations. Thermovoltage was measured by a $4\frac{1}{2}$ digit, HIL-2665 micro-voltmeter. The temperature gradient measurement was done with $3\frac{1}{2}$ digit, Agronic -113 DC microvoltmeter.

3.4.5 Optical absorption measurement:

The technique is utilised to know the type of transition and to estimate the absorption coefficient and forbidden energy gap of the material. The Bi_2S_3 films of thickness ranging between 0.1 um to 0.85 um were utilised for the optical absorbance study. The optical absorbance was measured as a function of wavelength. The photospectrometer, Hitachi Japan, was utilised at the scanning rate 100nm/min. in the wavelength range 500 nm. to 900 nm.

3.5 Design, Fabrication and Measurements on Photoelectrochemical (PEC) Cells.

3.5.1 Design and fabrication of a PEC cell :

The photoelectrochemical cell used in this investigations was fabricated in our laboratory and is shown in fig. 3.6 It consists of two test tubes, one hard glass test tube of the inner diameter 2.7 cm. and length 7 cm. approximately, and other ordinary test tube of the inner diameter 1.5 cm and length 12cm. The tubes were connected by

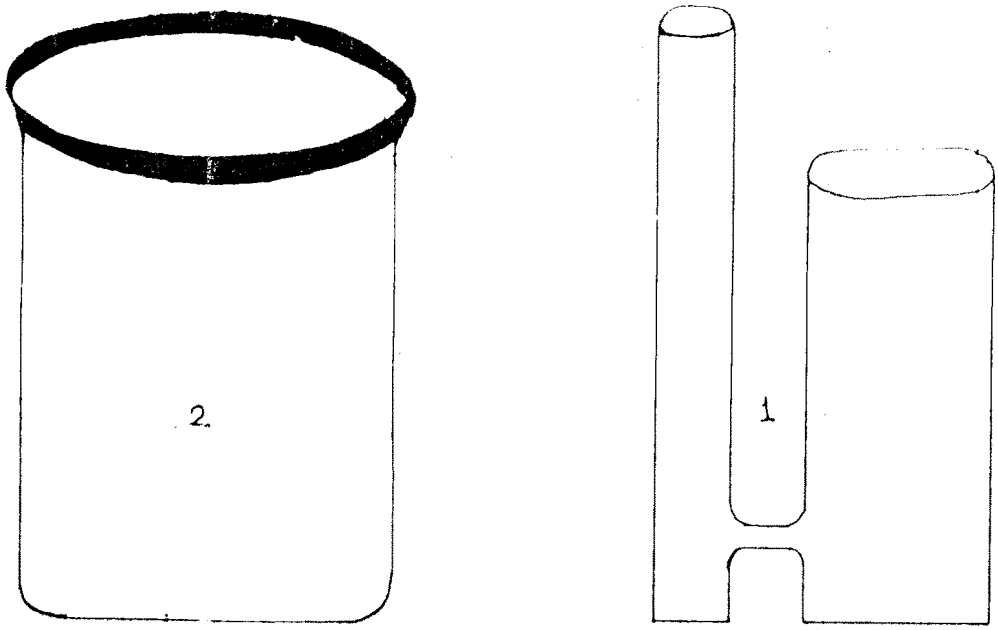

Fig.3.6 (a) Design constituents of a cell:
1) Glass cell,
2) Copper pot.

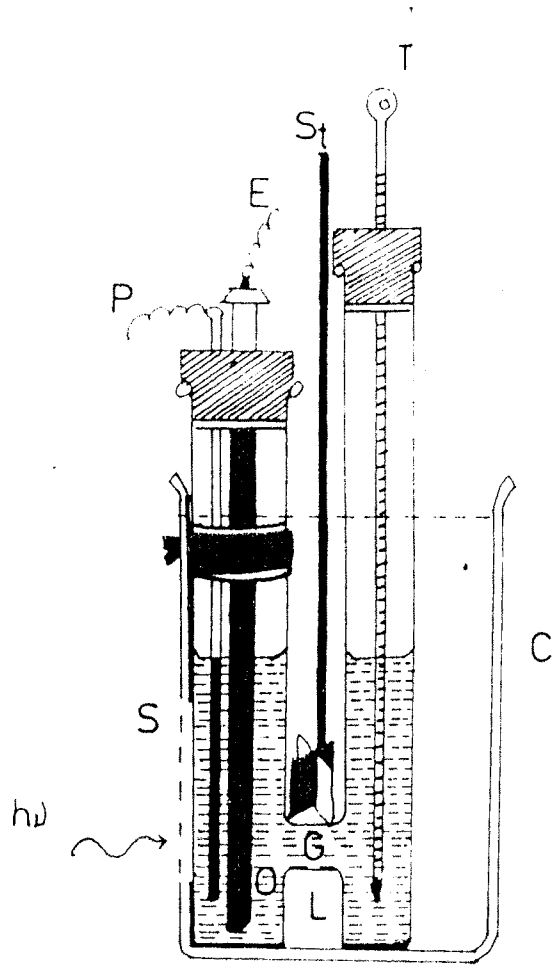

Fig.3.6(b) Fabrication of a PEC cell showing:
p- Photoelectrode,
E- Counter electrode
G- Glass Cell
C- Copper pot
S- Slit
S_t- Stirrer
L- Liquid electrolyte.

means of a capillary whose diameter equals approximately 0.5cm. This H-shaped assembly was fitted in a copper pot of a suitable size. A window of dimensions 2 x 0.5 cm was made for illumination of the photoelectrode.

The PEC cell was constructed by employing the Bi_2S_3 sample as a photoelectrode, a mixture of 1M NaOH-1M Na_2S-1M S as an electrolyte and a sensitised graphite rod as a counter electrode. The distance between a photoelectrode and a counter electrode was of the order of 0.3 cm. A rubber cork was used for air tightening of the cell and to support the counter and photoelectrodes. The active area of the sample was defined by a common epoxy resin. The sensitisation of a counter electrode was subjected to CoS treatment before use in PEC cell.

3.5.2 Measurements on PEC cell :

a) Nature of contact between Bi_2S_3 and the stainless steel:

The fabrication of an efficient PEC device requires an ohmic contact between the electrode material and the substrate. A contact is said to be ohmic, if it is noninjecting and has a linear I - V relation in both directions |90|. In practice, a contact is assumed to be ohmic, if voltage drop across it in either direction is negligible compared to that across the device, and hence does not perturb significantly the device performance. Actually the linearity of contact I-V relationship is therefore not important if the voltage is

small.

Hence the nature of contact between the Bi_2S_3 material and stainless steel substrate was examined. The sample on each substrate was mounted between two copper press contacts and I-V measurements were recorded as shown in fig. 3.7. The I-V relation was found straight line for both polarity indicating that the contact is ohmic.

b) Electrical and Optical characterisation of a PEC cell.

Design and contructional details of a PEC cell is outlined in section 3.5.1 . The electrical properties of a PEC cell can tell us about the charge transfer process across the electrode - electrolyte interface. In view of this, current - voltage characteristic in dark, power output curve , photo, and spectral responses were studied. This section gives the informations about the experimental arrangements for both electrical and optical studies of a PEC cell.

i) Experimental for electrical properties :

The circuitry as shown in fig.3.8 was used to study both I-V and C-V measurements. The applied junction potential was varied with a 10 turn 1K potentiometer and was noted with a Agronic, $3\frac{1}{2}$ digit, voltmeter, current flowing through the junction was noted with a HIL 2665,-$4\frac{1}{2}$ digit current meter. The cell was illuminated through a window by means of a 500 W bulb and care was taken against heating of the cell (water filter was interposed between the lamp and a cell).

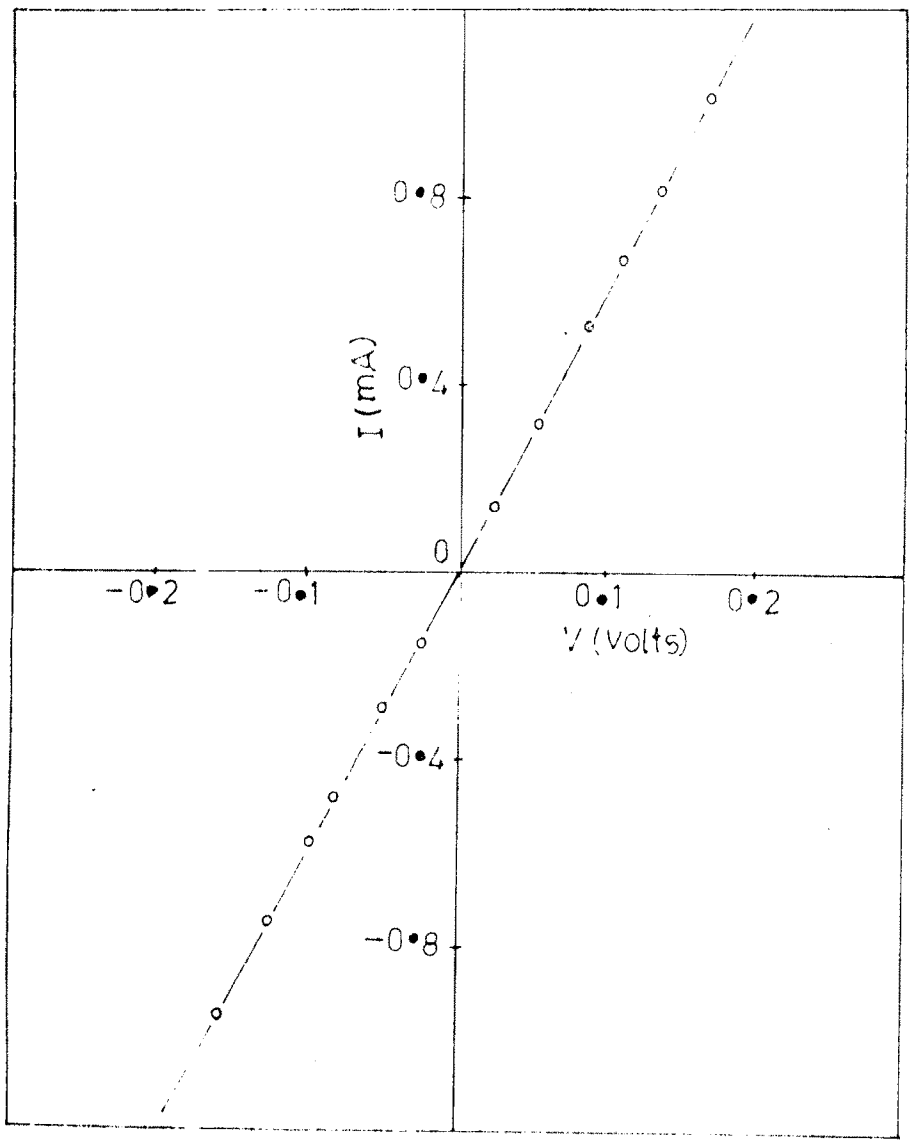

Fig.3.7. Nature of contact between Bi_2S_3 and Stainless Steel substrates.

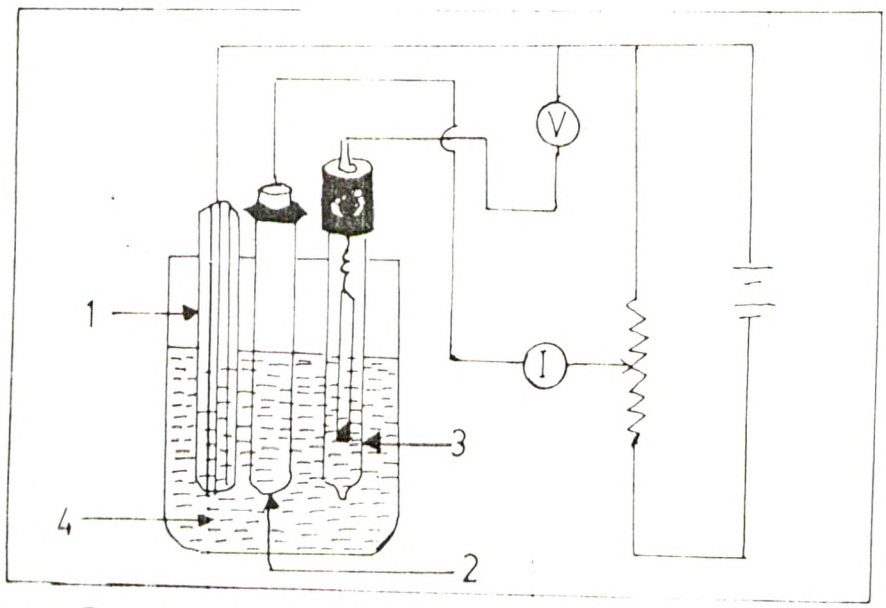

Fig.3.8 Experimental arrangement for electrical characterisation of a PEC cell:
1) Photoelectrode, 2) Counter electrode,
3) Saturated Calomel Electrode (SCE), 4) Electrolyte.

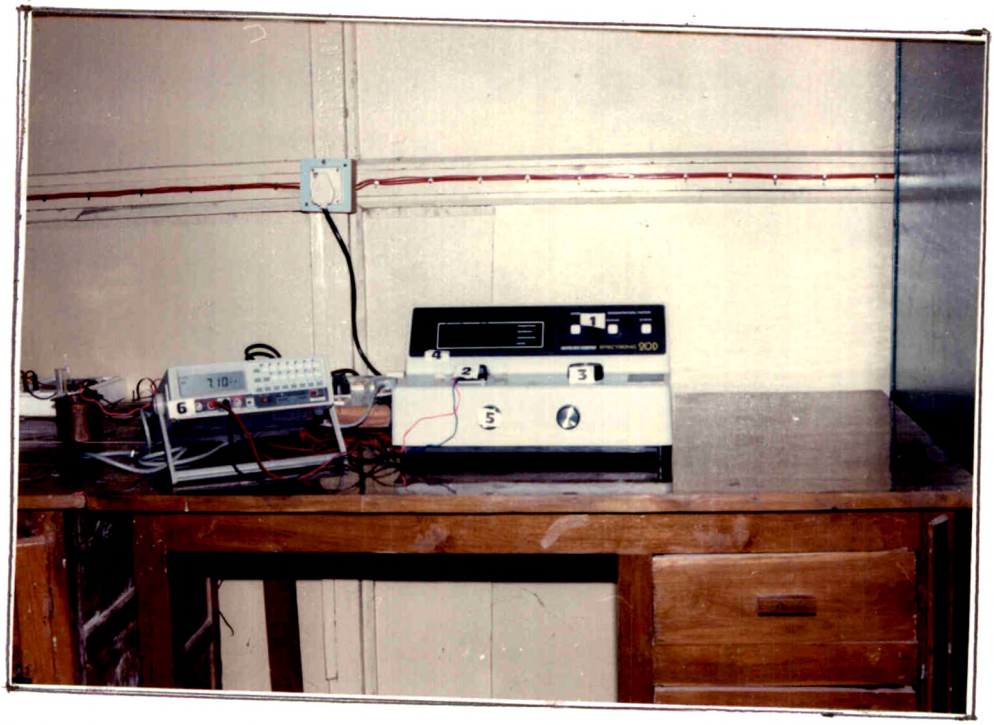

Fig. 3.9 Photograph of the exeperimental setup for spectral response of a PEC cell:
1) Photospectrometer, 2) PEC Cell, 3) Wavelength monitor, 4) Current meter, 5) Wavelength (nm),
6) Set zero and ON/OFF.

The C-V measurement was carried out (Vs.SCE) under reverse biasing of the junction by using the same circuit as above. The differential capacitance was measured by a Aplab-4910. capacitance meter at a superimposed 1 KHZ frequency and an a.c. voltage of 1 volt peak to peak.

ii). Experimental for optical properties. :

The measurements of a short circuit current and open circuit voltage for different intensities of illumination were carried out. The illumination was measured with a digital lux meter LX-101 (Lutron, Taiwan). The spectral response of a cell was recorded by using a photospectrometer (digispectronic,20 D,Milton and ROY, USA) in the wavelength range 400 nm to 1000 nm. A photograph of the experimental set up is shown in fig.3.9.