# CHAPTER - II

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## EXPERIMENTAL TECHNIQUES

## 2.1 Introduction

Theoretical background and detailed mechanism involved in both the thin films and photoelectrochemical solar cells are described in the respective chapters. As the recent progress in thin film formation and studies on their various properties have brought us closer to understand the microscopic basis of the surface science, this chapter is fully devoted to explain the necessary designs, fabrications and experimental techniques that are used for the preparation and characterisation of the semiconducting materials. Section 2.2 presents the procedural and technical details of preparation of the PbS and PbS:CuS thin films. The necessary designs and techniques for the electrical, optical and structural properties of thin film PbS and PbS:Cu are discussed in section 2.3. The design, fabrication and the essential experimental arrangements to characterise a PEC cell both electrically and optically are given in section 2.4.

## 2.2 Preparation of PbS:CuS Thin Films

Todays technology is required to develop new polycrystalline thin film materials using a variety of preparation techniques. The chemical deposition method has a special significance in this respect and therefore we employed it to deposit the PbS and PbS:CuS thin films /1-7/. The detailed procedure is as under:

### 2.2.1 Preparation of the substrates

The substrates used in the various stages of this work were spectroscopic grade amorphous glasses (microslides) and polished stainless steel strips. The stainless steel substrates were used for photoelctrochemical studies while the film properties were examined on the 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 mm x 25 mm x 2 mm). These were cut to a suitable size by means of a diamond point. The resulting size of the substrate was 72 mm x 10 mm x 2 mm.

### b) Preparation of the stainless steel substrates

The stainless steel sheet of a suitable size and guage was cut into strips of the size 72 mm x 10 mm x 0.5 mm and were used as the substrates. They were polished to a mirror grade quality by using (0000) polishing paper.

### 2.2.2 Substrate cleaning

As stickness of a film layer is directly dependent on cleanliness of the substrates, the key precaution is taken for the careful cleaning of the substrates before deposition. The following procedure was adopted while cleaning the substrates. The glass substrates were boiled in a chromic acid for about 20 minutes and washed with a tap water. They were further degreased in a medium concentrated teepol detergent solution and washed several times with a doubled distilled water and then with an ultrasonic cleaner.All the substrates were kept immersed in a double distilled water before use. In the similar fashion, stainless steel strips were first degreased in a mild teepol solution and then polished (mirror smooth) on a (0000) paper. Further procedure was similar to glass substrates except the use of chromic acid.

### 2.2.3 Preparation of the solutions

The different solutions used to prepare the PbS and PbS:CuS thin films were made in a doubly distilled water. The chemicals listed below were used for the purpose.

i) Lead acetate, AR-grade supplied by s.d.Fine -Chem Ltd; Bombay.

ii) Thiourea, AR -grade supplied by Chemo Fine Chemicals, Bombay (India).

iii) Sodium hydroxide, AR-grade supplied by Qualigen Fine Chemicals, Bombay.

iv) Copper sulphate, AR-grade supplied by s.d.Fine - Chem. Ltd; Bombay.

### 2.2.4 Deposition of PbS and PbS:CuS thin films

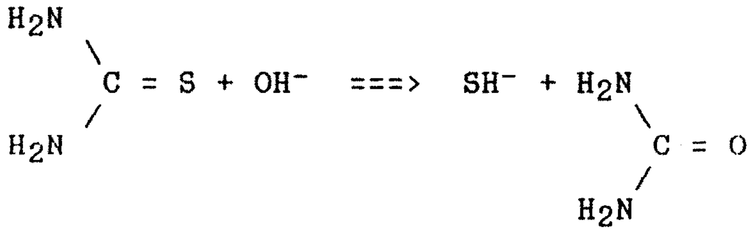
The deposits were obtained onto the spectroscopic grade microslide glasses at room temperature by using a chemical growth process. The starting materials used were freshly prepared aqueous solutions of the lead acetate, thiourea and copper sulphate. The procedure in brief was /6/. The thoroughly cleaned glass slides ~~kept~~ were adjusted vertically in a beaker consisting of 20 ml (0.5 M) lead acetate,20 ml (0.5 M) sodium hydroxide and 20 ml (0.5 M) thiourea solutions. The total volume of the solution was made roughly upto two third volume of a beaker by adding a double distilled water. For the preparation of PbS:CuS thin films, a controlled quantity of copper sulphate solution was added directly into the lead acetate solution. The copper concentration (x=0 - 0.8) was estimated by the volumetric control of the copper and the host solutions. The reaction was carried out at room temperature for a deposition time equal to 20 minutes. The samples were taken out from the beaker, washed in a double distilled water and then kept in a dark desiccator.

### 2.2.5 Mechanism of formation of PbS: CuS mixed thin films

The preparation of lead chalcogenides thin films by homogeneous precipitation from the solution is of considerable interest because it readily lends itself to large scale production /8/. The chemical deposition of lead sulphide films was first described by Hauser /9/ in 1910. The method involves the reaction of dilute solutions of thiourea with lead acetate. Almost all subsequent investigations dealing with the chemical deposition of lead sulphide essentially have employed modification of Hauser´s method. The principle variation have involved changes in the concentrations of lead acetate and thiourea solutions used, the temperature of depositions and the use of surface seeding nuclei as a means of improving the properties of the films. The film formation in homogeneous precipitation reaction is found to be influenced by the rate of diffusion of colloidal particles to the glass surface and the influence of crystallising nuclei which can be formed by the addition of metal ions whose sulphides are extremely insoluble (sulphides of Ag, Hg, Pt and Au) /9/.

The physico-chemical mechanism underlying the chemical deposition of metal chalcogenides out of an alkaline medium in terms of their hydroxide complex have been discussed by Rainthala et al /1/, Kicinski /11/ and Mondal et al /12/.In the present investigation the lead sulphide thin films were deposited from a chemical bath consisting of equimolar solutions of lead acetate and thiourea in the presence of sodium hydroxide. The lead acetate and thiourea solutions were mixed at room temperature and NaOH was added to adjust the pH around /1,6/; The basic reactions are:

i) Thiourea hydrolyzes in an alkaline medium to give $S^{2-}$ ions



$$(H_2N)_2C=S + OH^- \Longrightarrow SH^- + (H_2N)_2C=O \qquad \ldots(2.1)$$

$$HS^- + OH^- \Longrightarrow H_2O + S^{2-}$$

ii) $Pb(CH_3COO)_2 + S^{2-} \Longrightarrow PbS + 2CH_3CO\bar{O}.$ ...(2.2)

This happens only when the ionic product (IP) of $Pb^{2+}$ and $S^{2-}$ ions exceeds the solubility product (SP) of PbS. The ratio of, IP/SP = S, defines the supersaturation of the ions over the PbS and can be varied by choosing appropriate initial concentrations of the reaction. When S>1, the ions combine on the substrate and in the solution to form PbS nuclei which grow with time to give film and precipitate, respectively. Once PbS is formed it acts as catalyst for further deposition of fresh portions of PbS preferentially. The rate of deposition and terminal thickness is dependent on the reaction mixture since the later determines the rate of formation and growth of nuclei. As the catalytic PbS surface develops both on the surface and in volume of the solution, the properties of PbS formed on the substrate is determined by the ratio of nuclei formed on the substrate and in the overall solution. At low supersaturation, (S<1), the existance of foreign particles on the nucleating surface will act as nuclei for PbS formation (for low concentrations) which then grow to larger sizes. The nuclei grow and coalesce to form a continuous film, the rate of deposition is initially high because the concentration of $Pb^{2+}$ and $S^{2-}$ is high. As more and more PbS is formed, the solution becomes depleted of ions resulting in a lower rate of deposition. The rate of deposition is zero resulting in terminal thickness when the concentration of $Pb^{2+}$ and $S^{2-}$ ions decrease to a value such that $S < 1$. The quality of the films formed is dependent on the several preparative parameters such as pH of the reaction, temperature of the deposition, sulphur ion concentration hence on Pb:S ion ratio and the nature of the substrate material.

### 2.3 The Techniques of Thin Film Characterisations

#### 2.3.1 The thickness measurement

The weight difference density method in which mass, area and density of the material were considered, was used for the measurement of thickness of the films. The film thickness is related to the mass,area and density of the material as:

$$t = \frac{m}{A \, . \, d} \qquad \ldots . \ (2.3)$$

where, m = weight in grams of the film,

A = area of the film in $cm^2$, and

d = density of the material in $gm.cm^{-3}$

#### 2.3.2 The X-ray diffraction and SEM studies

The X-ray diffraction patterns were obtained on these films using a Philips - 1710, X-ray diffractometer with $CuK_{\alpha}$(1.5405 A°) radiation. The angle range of scanning was from 5° to 100°. The scanning electron micrographs (SEM) of these samples were obtained with a scannning electron microscope, Stereoscan, 250 MK(III) Camb., Instruments Ltd, U.K.

### 2.3.3 Design and measurements on electrical conductivity

The electrical conductivity of the samples in dark was measured by a conductivity measuring unit designed in our laboratory as shoown in figure 2.1 (a). It consists of two brass plates of the size 10 cm x 5 cm x 0.6 cm, one of the plates is fixed tightly on a asbestos base of the dimension 10 inches 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 sandwitched in between 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 the achieve the electrical insulation from either of a brass plates. A sample holder of the dimensions 3 cm x 0.5 cm x 0.6 cm was designed and permanently fixed at the centre of the upper plate. A sample whose electrical conductivity was to be measured was mounted with the copper press contacts below the sample holder.The area under consideration was defined with the rest sample area erased. The sample was electrically insulated from the upper brass plate and sample holder by interposing the mica pieces at the proper places. Thermal radiation losses were reduced by covering the whole set up in a bakellite box. The box was coated from 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 brass plate. An Aplab regulated power supply unit was used to pass the current

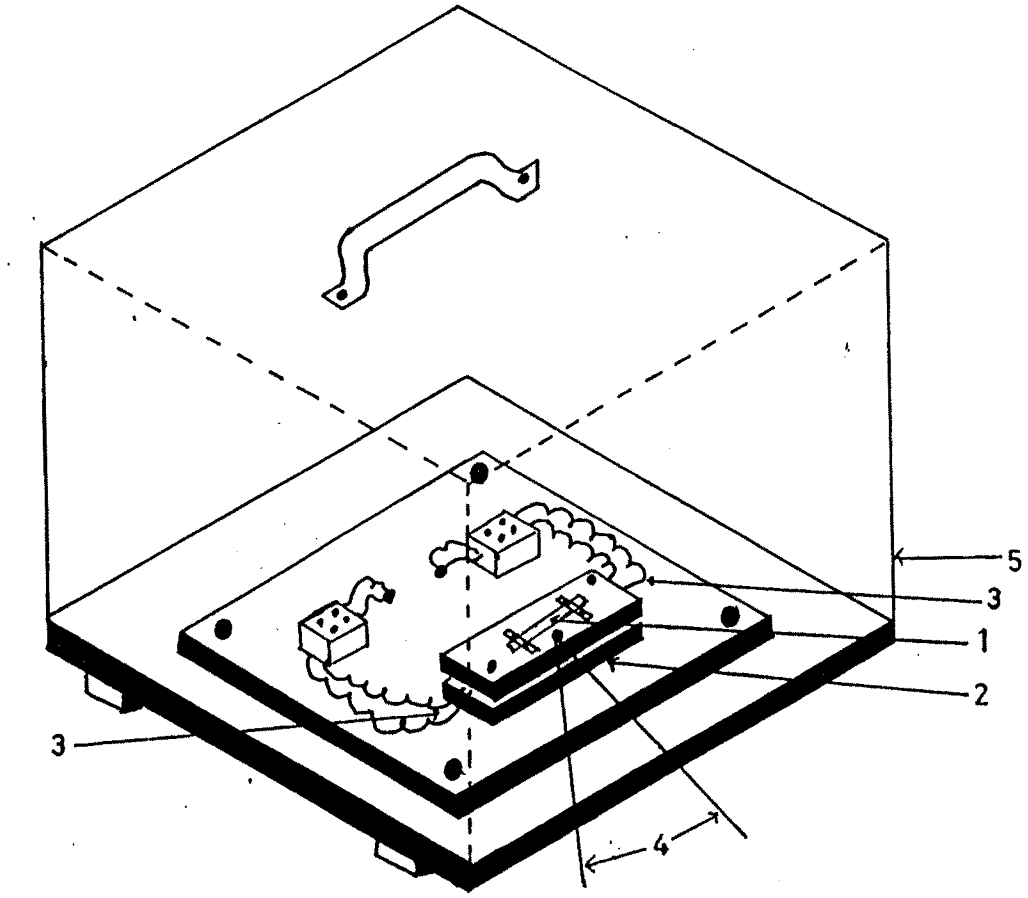


Fig. 2.1(a) Design for the measurement of an electrical conductivity.

1) Sample,
2) Brassplates,
3) Electrical heaters,
4) Thermocouple,
5) Shield.

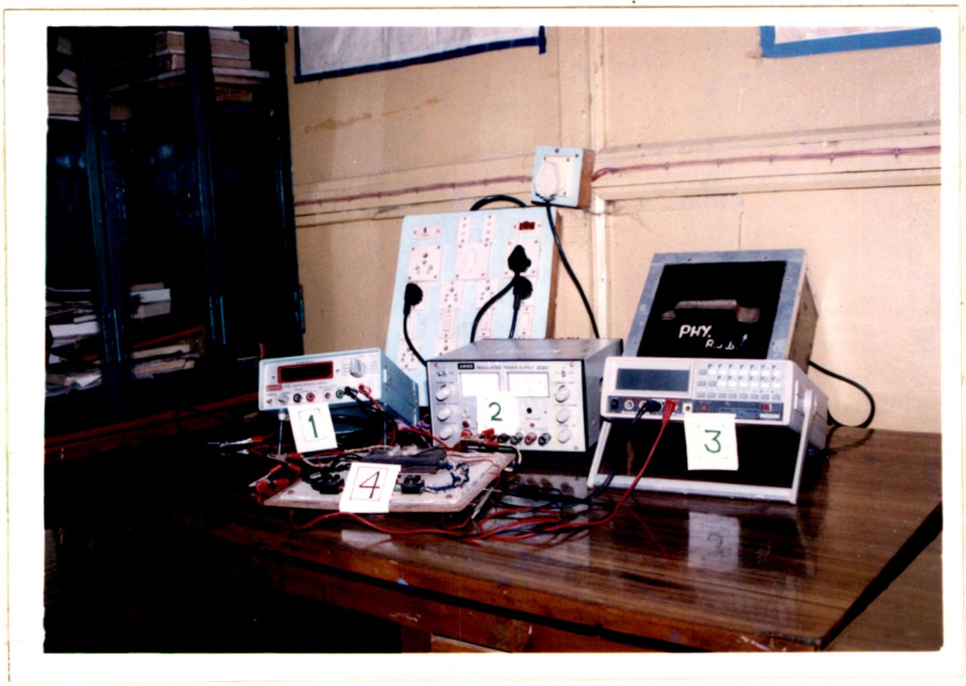


Fig. 2.1(b) Experimental arrangement for the measurement of conductivity,

1) Microvoltmeter,
2) Power supply,
3) Current meter,
4) Conductivity unit.

through the sample. The potential drop across the sample was kept constant and the current through the sample was noted with a sensitive HIL - 2665, 4 1/2 digit current meter. A photograph of the necessary experimental set-up for the measurement of the conductivity is shown in figure 2.1 (b).

### 2.3.4 Design and measurements on thermoelectric power (TEP)

The necessary conditions and requirements for the thermoelectric power measurements have been discussed by Bauerie et al /13/. Figure 2.2 shows the schematic of the TEP unit. It consists of two copper plates of the dimensions 5 cm x 4 cm x 1.2 cm which are fitted on the asbestos sheet supported by a bakellite sheet. The plates were arranged in parallel with a distance of 5 cm separation. The plates were pitched from the bottom to a size of the miniheater and the miniheaters of the different wattage (65 W and 35 W) were fixed in them. The necessary care was taken for 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 was fixed lengthwise on the top adjacent nearer edges of the copper blocks. The sample size used in this study was 5 x 0.5 cm on amorphous glass substrate and the dimensions of the substrate holder were 3 x 0.5 x 0.5 cm. The sample was electrically insulated from copper blocks and the substrate holder by means of the mica pieces. The copper press contacts were used for the measurement. A Cr-Al thermocouple (24 guage) was fixed on the top of the copper blocks to sense the working temperature. The proper

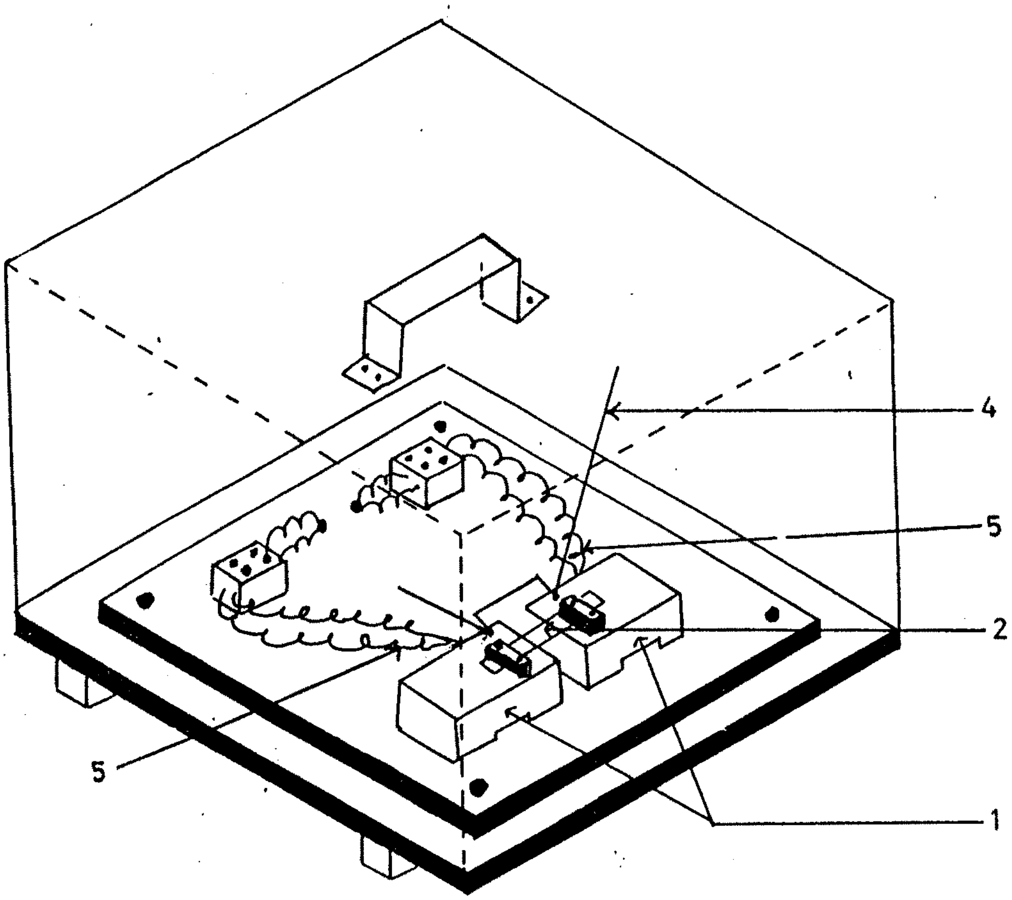


Fig. 2.2 Design for the measurement of TEP

1) Copper blocks,
2) Sample,
3) Thermocouple (mean temperature recorder),
4) Differential thermocouple (Thermovoltage recorder),
5) Heaters.

shielding of the unit was made by a bakellite box to minimize the thermal radiation losses. Thermovoltage was measured by a HIL - 2665, 4 1/2 digit microvoltmeter. The temperature gradient was measured with a Agronic - 113, 4 1/2 digit microvoltmeter.

### 2.3.5 Optical absorption measurements

The technique is utilised to estimate the absorption coefficient and forbidden energy gap of the semiconducting materials. It also gives the useful information about the type of transition. The measurements on optical density as a function of wavelength from 5000 A°-26000 A° were performed by using a spectrophotometer,Hitachi -330 (Japan). The scanning speed was 120 nm/min with a chart format of 50 nm/cm.

## 2.4 The Techniques of Photoelectrochemical(PEC) Characterisations

### 2.4.1 Design and fabrication of a photoelectrochemical cell

The photoelectrochemical cell used in these investigations was fabricated in our laboratory and is shown in figure 2.3. It is a H-shaped tube fitted in a copper pot of a suitable size. A window of the size 2 cm x 0.5 cm was made for illumination of the photoelectrode material.

In actual, the cell consists of PbS:CuS sample as a photoelectrode, a mixture of equimolar NaOH -S-$Na_2S$ as an electrolyte and sensitised graphite rod as a counter electrode. The photo and counter electrodes were kept at a distance of 0.3 cm. They were fitted by means of a rubber cork. The active area of the sample was defined by a common epoxy resin. The sensitisation of a counter electrode was done with a CoS solution for 24 hours before use in photoelectrochemical cell.

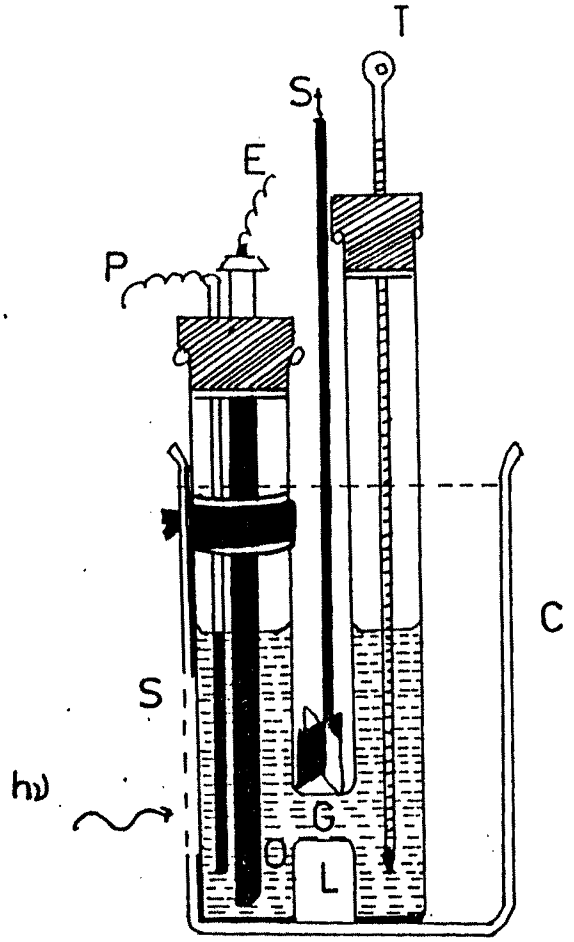


Fig. 2.3 Fabrication of a PEC cell

P - Photoelectrode
E - Counter electrode
G - Glass cell
C - Copper pot
$S_t$ - Stirrer
L - Liquid electrolyte
S - Slit.

### 2.4.2 Measurements on photoelectrochemical cell

#### a) Electrical contact between a substrate and a PbS:CuS thin film

An ohmic contact between the electrode material and the substrte is essential for the fabrication of an efficient photoelectrochemical device. A contact is said to be ohmic if it is noninjecting and has a linear I-V relation in both directions. In practice, a contact is assumed to be ohmic, if voltage across it in either direction is negligible compared to that across the device and hence does not perturb the device performance significantly. Actually, linearity of the contact I-V relationship is therefore not important if the voltage is small. The nature of the contact between PbS:CuS material and stainless steel was therefore examined.

The sample was mounted between the two copper press contacts and the current-voltage measurements were recorded. The I-V relation was found to be a straight line for both type of polarity indicating that PbS:CuS offers ohmic contact to stainless steel. The contact resistance was estimated and is only a few ohms in our case.

#### b)Electrical and optical characterisation of a PEC cell

The design and constructional details of the photoelectrochemical cell are outlined in the section 2.4.1. The electrical properties of a PEC cell give us insight about the charge transfer processes across the electrode/ electrolyte interface. Therefore, the current-voltage characteristic in dark and in light, power output curve, photo speed and spectral responses were studied. This section deals with the experimental arrangements for both electrical and optical studies of a photoelectrochemical cell.

**i) The electrical properties**

The current-voltage and capacitance-voltage measurements were carried out using a circuit diagram as shown in figure 2.4. The applied junction potential was varied with a 10 turn, 1K linear potentiometer and was noted with a Agronic -113 4 1/2 digit voltmeter. The current flowing through the junction was noted with a HIL -2665, 4 1/2 digit current meter. The cell was illuminated through a window by means of a 250 W bulb and care was taken against heating of the cell (water filter was interposed between the lamp and the cell). The C-V measurements were performed under reverse biased condition of the junction. The above circuit was used for this purpose. The differential capacitance was measured by an Aplab-4910 autoranging digital display capacitance meter at a superimposed frequency of 1 KHz. The superimposed AC voltage was 1V - pp.

**ii) The optical properties**

The measurements of a short circuit current and an open circuit voltage for different intensities of illumination was carried out. The illumination was measured by an Aplab - 101 digital lux meter.

The open circuit voltage was also measured for various ON and OFF times of a cell. The ON and OFF times refer to the time for illumination and cut off, respectively.

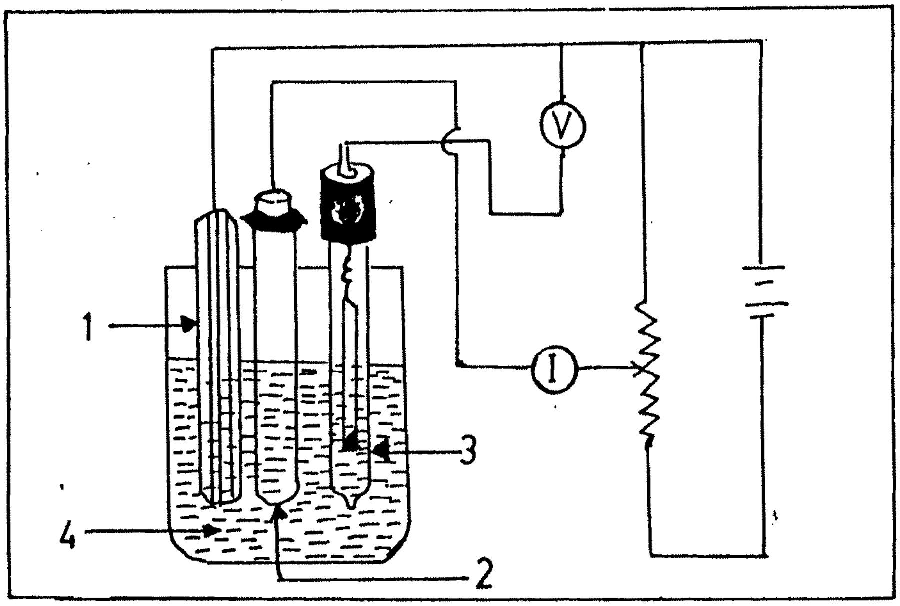


Fig. 2.4 Circuit arrangement for electrical characterisation of a PEC cell

1) Photoelectrode
2) Counter electrode
3) Saturated calonel electrode (SCE)
4) An Electrolyte.

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