C H A P T E R – V

PHOTOELECTROCHEMICAL CHARACTERIZATION OF SPRAYED WO$_3$ THIN FILMS

CHAPTER-V

PHOTOELECTROCHEMICAL CHARACTERIZATION OF SPRAYED TUNGSTEN OXIDE THIN FILMS

5.1 INTRODUCTION :

Research on photosynthesized reactions at semiconductor electrodes, aimed toward the photodecomposition of water and the construction of photoelectrochemical cells for use in solar energy conversion devices. Suitable electrodes should be easily prepared, stable over long time periods of operation and have a optimum band gap to allow efficient utilization of the solar energy spectrum. Stable electrodes, such as TiO_2, WO_3 are large band gap materials (Eg $\geqslant$ 2.8 eV) while materials with smaller gaps tend to be unstable in aqueous electrolytes.

Photoelectrochemical cells can offer some advantages over purely solid state devices for the construction of photovoltaic cells; however, photoelectrochemical methods can also be powerful tools for the measurement and evaluation of the material properties of semiconductor of interest. It is the latter that will be the main topic of interest of this work.

Many investigations of the films of WO_3 have been carriedout concerning its photoelectrochemical properties. The films were prepared usually by vacuum evaporation [1], chemical vapour deposition [2], sputtering [3], thermal oxidation or anodic oxidation of metallic tungsten plates [3,4]. However, very

few reports are available on the films of tungsten oxide prepared by spraying solutions onto hot substrates [5]. In this chapter we report photoelectrochemical behaviour of the cell formed with WO_3 thin films as semiconducting photoelectrode. The different parameters such as flat-band potential, junction ideality factor, decay time constant are estimated.

5.2   EXPERIMENTAL :

Tungsten oxide films deposited on F-dopped tin oxide coated glass substrates were used for this study. Films prepared with 0.01 M concentration of spraying solution were utilized. Photoelectrochemical cell was then fabricated by employing WO_3 thin films as a photoanode, 0.1 M Na_2SO_4 solution as an electrolyte and graphite rod as a counter electrode. The photoelectrochemical measurements were performed using a 80 watt mercury vapour lamp and interference filters. The capacitance measurements were carried out by using Aplab 4910, LCR bridge and the voltages were measured with respect to saturated calomel electrode. The illuminometer model 5200 (Kyoritsu Electrical Instruments Works Ltd., Japan) was used for the intensity measurements. Transient photoresponses at different illumination intensities were recorded with RE 2000 X-Y recorder. A silver paste was applied to F.T.O. coated glass substrates to ensure ohmic contacts.

5.3   RESULTS AND DISCUSSION :

5.3.1 Current-Voltage Characteristics :

Photoelectrochemical properties of the films were studied by illuminating WO_3 — electrolyte junction with 80 watt mercury
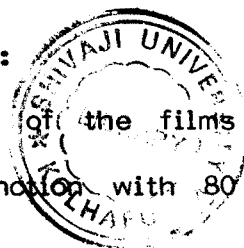
vapour lamp. I-V characteristics were obtained in the dark and under different illumination intensities. These I-V plots are shown in Fig.5.1 which indicates that the junction between films and electrolyte is rectifying in nature. Magnitudes of I_{sc} and V_{oc} at 28 mW/cm^2 illumination intensity were 12 $\mu A/cm^2$ and 260 mV, while fill factor and energy conversion efficiency (η) were of the order of 0.28 and 0.003% respectively. Being large band gap ($\sim$ 2.8 eV)semiconducting material this low value of η is obvious. However, the values of short circuit currents and open circuit voltages obtained were approximately same as reported by others [3,5]. It is found that no report is available on magnitude of fill factor. Although WO_3 material has low solar energy conversion efficiency, our interest in this material is due to its long term stability in aqueous electrolytes.

Values of I_{sc} and V_{oc} for different illumination intensities were also obtained and the variation is shown in Fig.5.2 It is found that I_{sc} is directly proportional to the light intensity. This linear relationship can be understood in terms of Schottky barrier theory, while non-linear relationship between V_{oc} and illumination intensity was observed.

Fig.5.3. shows variation of log I versus V of the junction in forward bias condition. Ideality factor for the cell in dark and under illumination with intensity 28 mW/cm^2 were found to be 9 and 5 respectively. This high value of ideality factor is attributed to the presence of surface states and polycrystalline nature of the material.
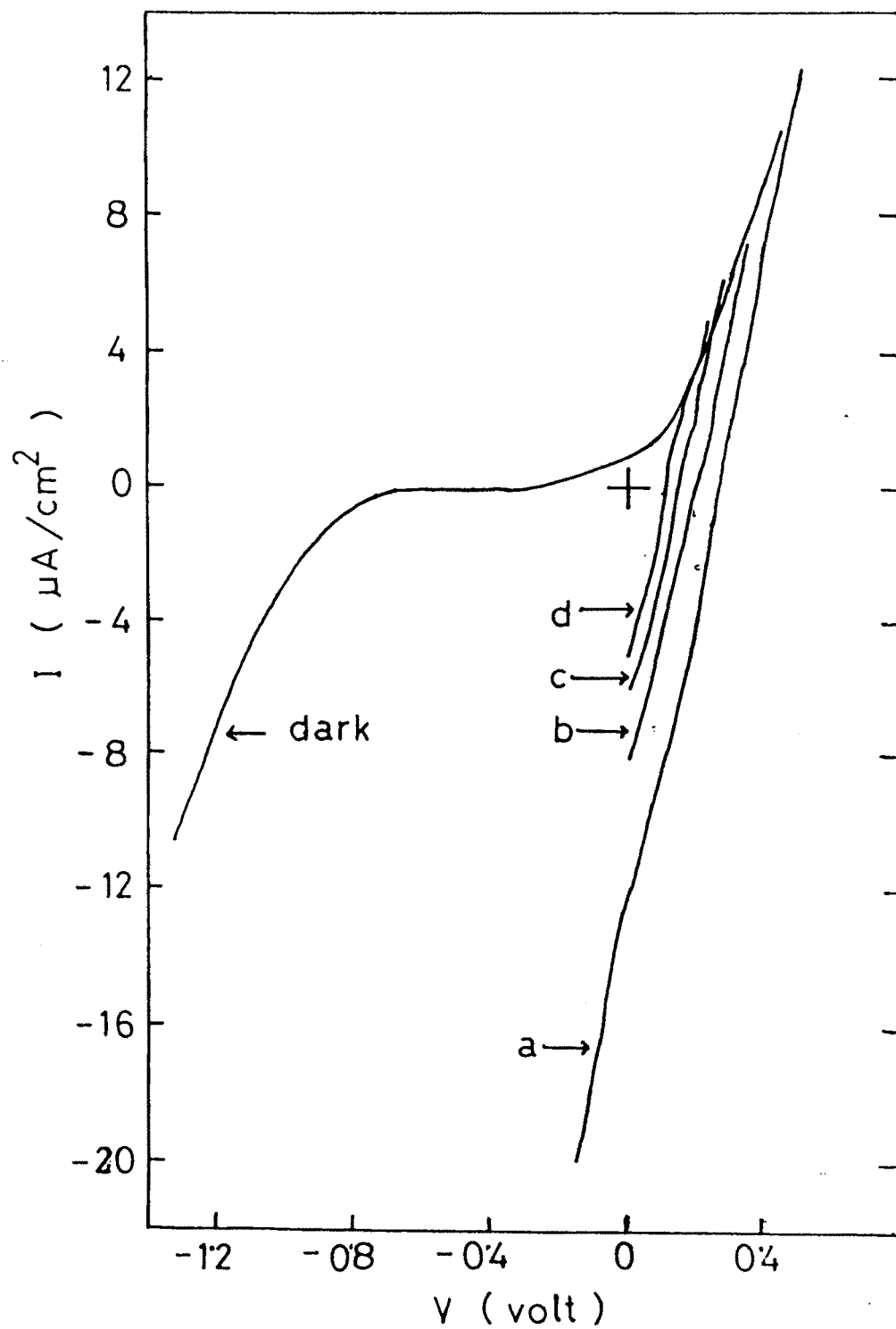
Fig.5·1   Current   vs.   potential   curves   for   WO$_3$
photoanode   in   dark   and   on   illumination   with
intensity : (a) 28 mW/cm^2 (b) 18 mW/cm^2
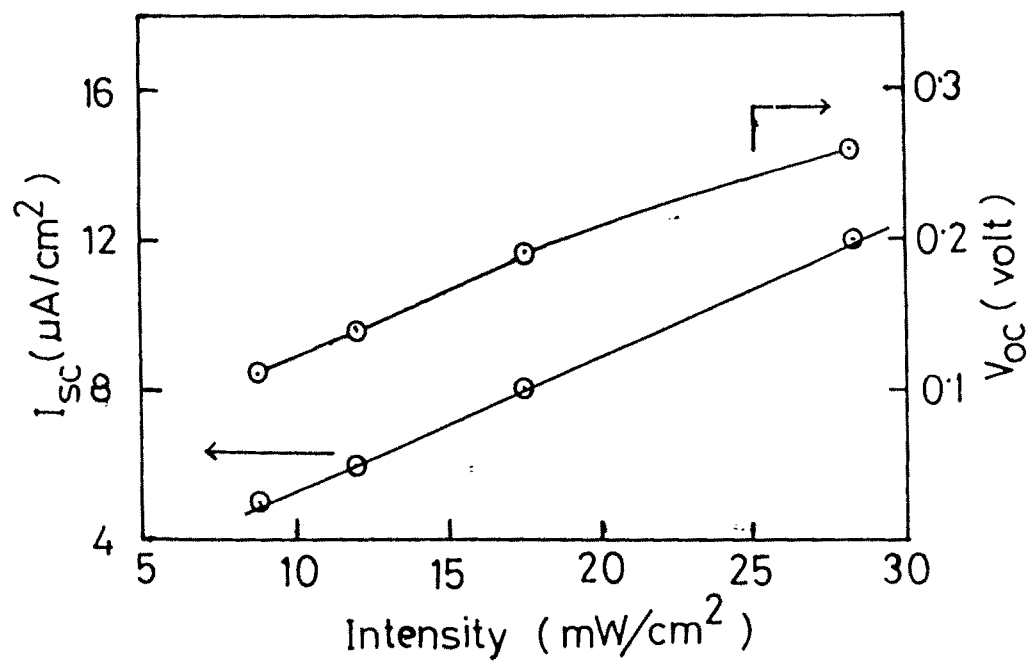(c) 12 mW/cm^2 and (d) 8 mW/cm^2.

Fig.5·2   Variation of short circuit current and open
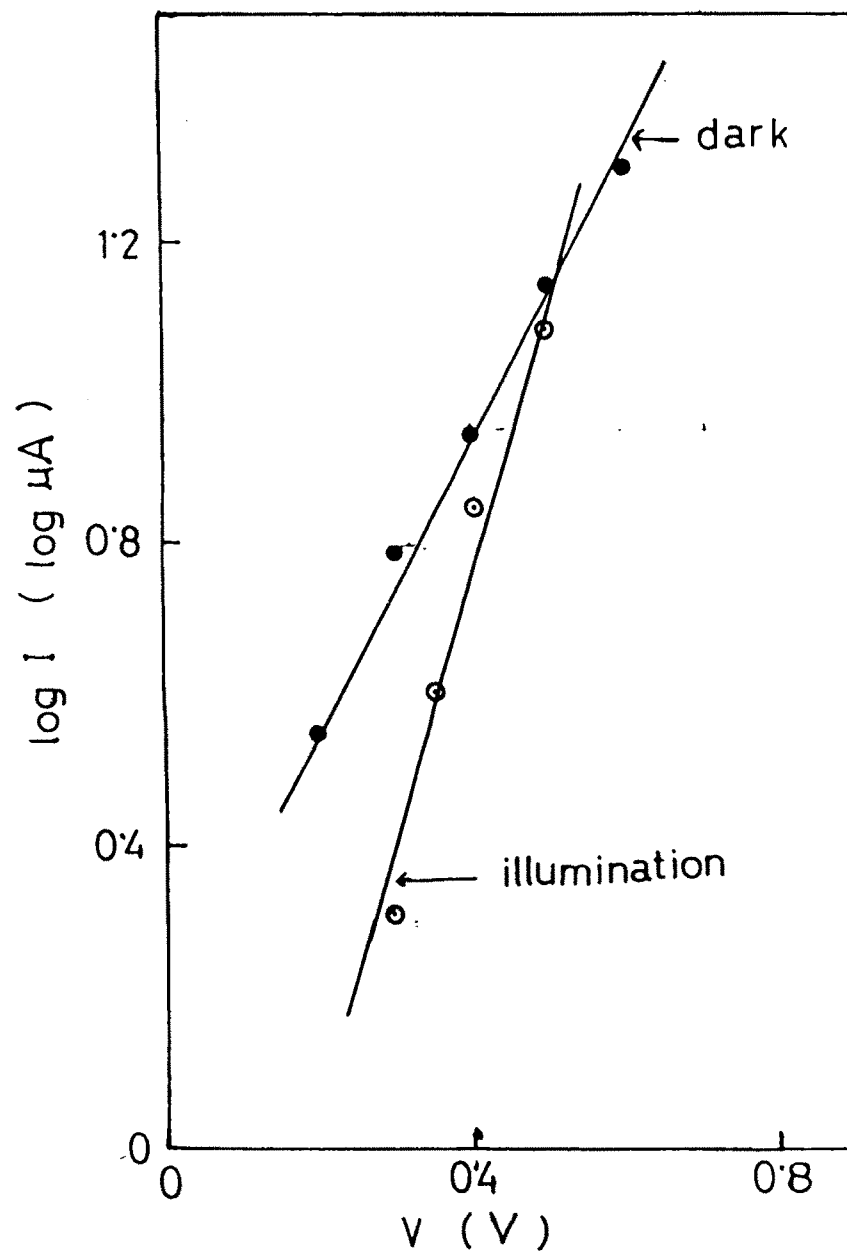circuit voltage with the light intensity.

Fig.5·3   Variation of log I versus V   a) in dark
and b) under illumination with intensity
28 mW/cm^2.

5.3.2 SPECTRAL RESPONSE :

Fig.5.4 shows the spectral distribution of the photocurrent. It is seen that, the photocurrent shows peak at 375 nm beyond which it decreases contineously. The onset of the photocurrent occurs at about 450 nm corresponding to thé band gap energy of 2.8 eV. Similar results are reported by W.H.Strehlow et al [6].

5.3.3 TRANSIENT PHOTORESPONSE :

The decay time constant of the photogenerated excess minority carriers is an important parameter in solar cell design [7]. The variation of open circuit voltage decay technique which was originally introduced by Gossick [8] and subsequently studied by several others [13-15]. This technique has recently been applied to semicondctor-electrolyte interfaces. Horzion et al [9], studying CdSe/polysulphide cells, reported fast photocurrent transients on nanosecond time scales. Ramprakash et al [10] reported transients on milliseconds time scale for $n\text{-}InP/Fe(CN)_6^{-3/-4}$ cells, while Lokhande and Pawar [11], Chougule and Pawar [12] and Patil et al [16] reported photovoltage decay periods on second time scales for their cells formed with CdS/polysulphide, Ti-Ni-Oxide/NaOH and Fe_2O_3/KOH respectively. Fig.5.5 shows the variation of transient photovoltages with illumination intensity. Differences in the heights and detailed shape of these curves are due to differences in the initial injection levels. The decay time constant τ_{off} can be defined by the equation,
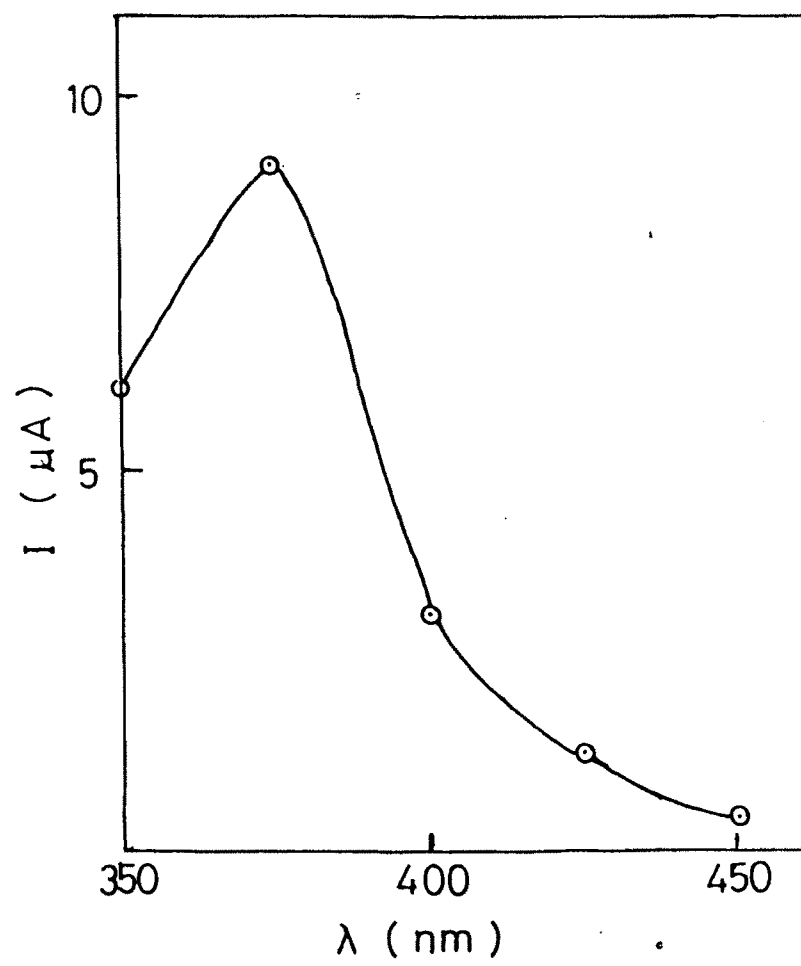
$$V_{ph} = K.e^{-\frac{t}{\tau_{off}}}$$
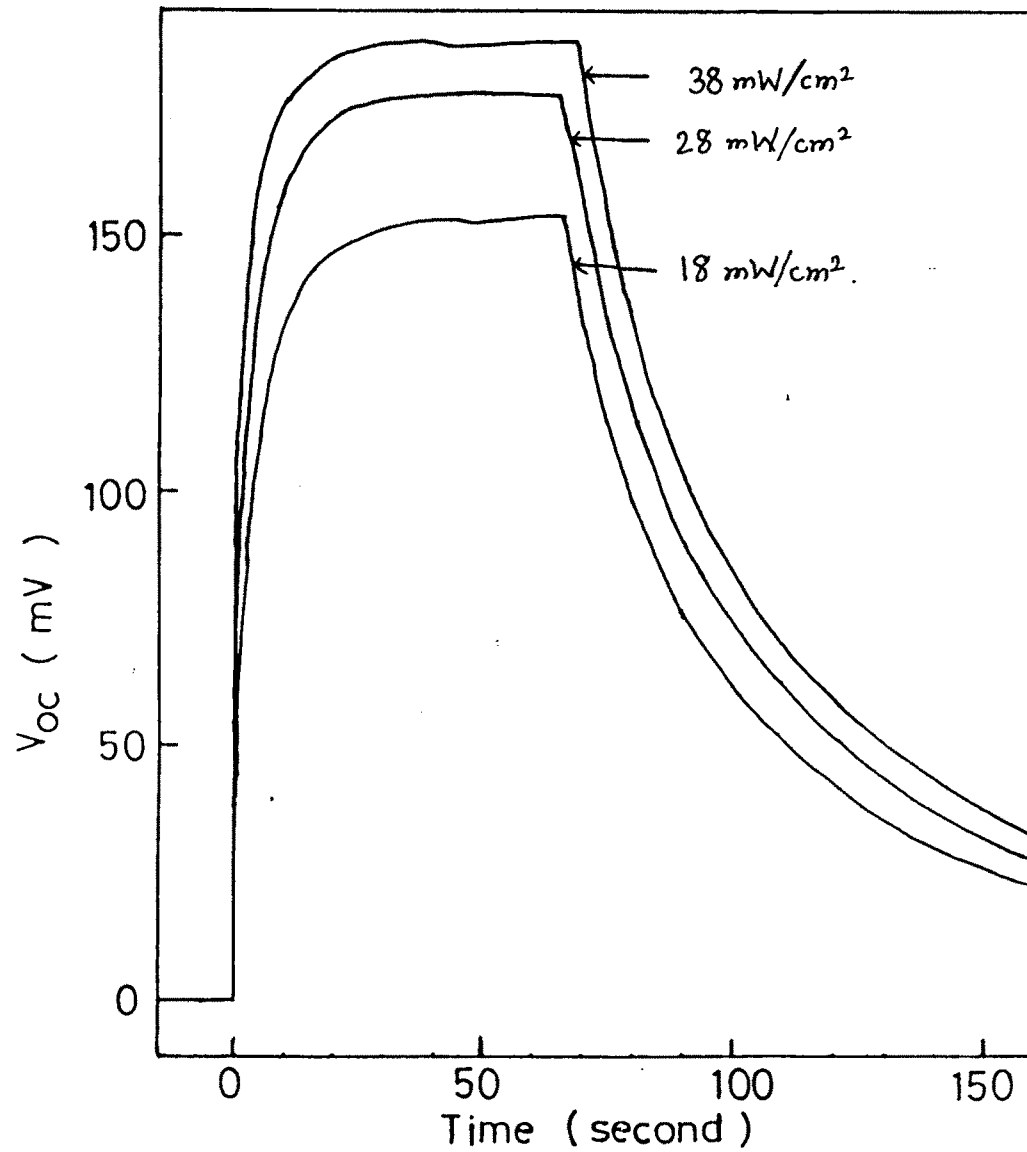
Fig.54   Spectral distribution of photocurrent.

Fig.5.5 : Variation of transient photovoltaes with different illumination intensities

where 'K' is a constant and 't' is the time in seconds. Thus τ_{off} has been calculated for different light intensities and were 34s, 36s and 38s for intensities 18,28 mW/cm^2 and 38 mW/cm^2 respectively. Generally for metal oxides, a slow decay in V_{oc} may be attributed to slow charge transfer kinetics at the interface and slow release of charges from slow surface states. It is observed that, the decay time constant at higher intensity is larger indicating the slower hole capture kinetics. _

5.3.4 CAPACITANCE-VOLTAGE CHARACTERISTICS :

The capacitance of the WO_3 — electrolyte interface was measured at different electrode potentials by using LCR bridge. It is found that the capacitance decreases with increasing electrode potentials.Fig.5.6 shows the Mott-Schottky plot for the film-electrolyte interface. The flat-band potential determined by extrapolating the Mott-Schottky plot at $1/C^2$ =0 was 0.15 V versus SCE. Many workers have reported different values of V_{fb} for WO_3 films in different electrolytes. It is concluded however, that this value depends mainly on the method of electrode preparation and electrolyte used. From the slope of the Mott-Schottky plot the value of donor density was calculated to be 5 X 10^{16} cm^{-3} .

5.3.5 STABILITY :

For a material to be used in practical devices, good stability is required including small tendency to dissolve directly or under illumination, stability against photo-oxidation
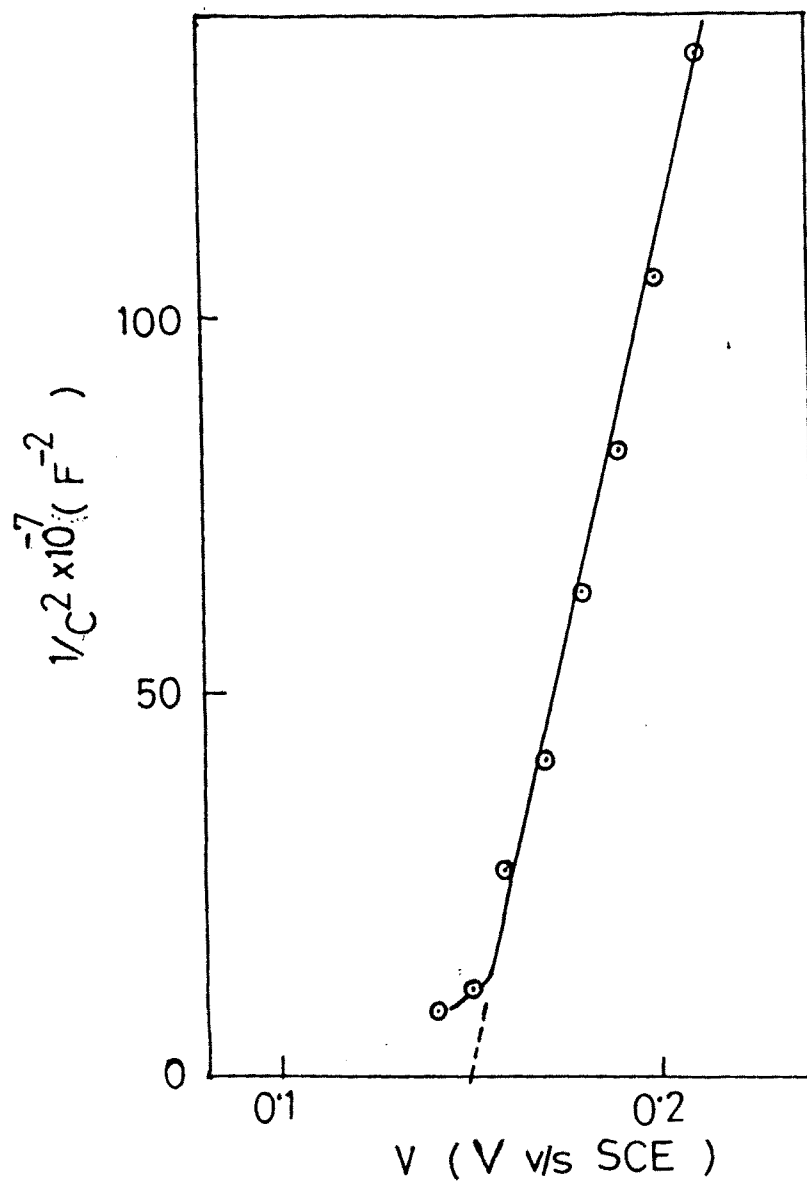
Fig.5·6   Mott-Schottky   plot   for   film-electrolyte junction.

for n-type materials.Fig.5.7 shows the variation of short circuit current with time. It is found that I_{sc} decreases by about 30% in the first 20 min. and then remains constant for 10 or more hours in 0.1 M Na_2SO_4 electrolyte.
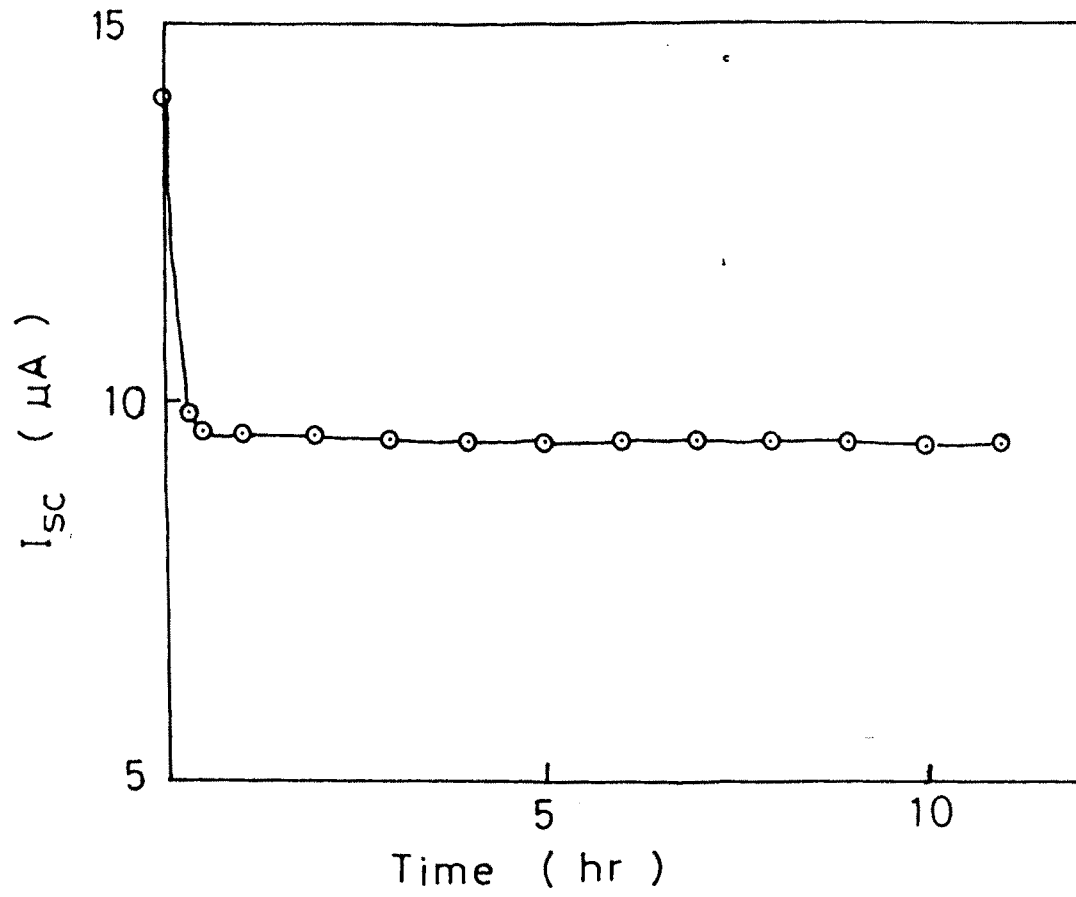
Fig. 5.7 : Variation of short circuit currecnt with time.

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