C H A P T E R –VI

ESTIMATION OF PHYSICAL PARAMETERS OF THE PEC CELL FORMED WITH WO_3 PHOTOANODE BY USING GARTNER'S MODEL

CHAPTER-VI

ESTIMATION OF PHYSICAL PARAMETERS OF THE PHOTOELECTROCHEMICAL CELL FORMED WITH WO_3 PHOTOANODE BY USING GARTNER'S MODEL

6.1 INTRODUCTION :

Tungsten oxides, unlike tungsten chalcogenides, are less studied materials specifically for its use as a photoanode in photoelectrochemical cells. As, for the semiconducting properties of WO_3 ,different values of band gap energy and flat band potentials, have been reported by different authors [1-7]. A large influence on both parameters seems attributable to the different preparation techniques. The variation in band gap energy and flat band potential could be explained by the amorphous or crystalline nature of WO_3 ,the presence of surface states and to the different measuring techniques. The density of the surface states as well as its distribution in the energy within the band gap is known to be very sensitive both to the different preparation techniques of the electrodes and to the semiconductor-electrolyte interface [8]. Therefore, it is of interest to estimate these parameters for WO_3 thin films prepared by spray pyrolysis technique.

The physical parameters such as band gap energy (E_g) of a semiconductor, concentration of carriers (N_D),flat band potential (V_{fb}) etc. could be determined by photoelectrochemical technique [9,10]. In fact, Gartner's model

of the metal-electrolyte junction can also provide a successful physical description of the semiconductor-electrolyte interface with both single crystals and polycrystalline electrodes [11]. In this investigation we have used Gartner's model for the estimation of different parameters of PEC cell; formed with sprayed WO_3 thin film.

6.2 EXPERIMENTAL :

The WO_3 thin films prepared by spraying 0.04 M solution on to F.T.O. coated glass were used for this study. A photoelectrochemical cell was formed using WO_3 films as a photoanode, 0.1 M Na_2SO_4 as an electrolyte and graphite rod as a counter electrode. A saturated calomel electrode (SCE) was used as a reference electrode. The silver paste was applied to ensure ohmic contact with the substrate. A 80 watt mercury vapour lamp was employed to illuminate the cell. Interference filters were used to obtain monochromatic light. The current through the circuit and voltage applied to the cell were measured by (input) nanoameter and digital D.C. voltmeter respectively. The illuminometer model 5200 (Kyoritsu Electrical Instruments Works Ltd., Japan) was used for the intensity measurements.

6.3 RESULTS AND DISCUSSION :

The PEC cell was fabricated by employing these films as photoanodes. The cell configuration was as follows,

$$n - WO_3/0.1\ M\ Na_2SO_4/C.$$

The cell was then illuminated with filtered light from mercury vapour lamp and photocurrents at different reverse bias voltages were recorded for different wavelengths.

Under the assumptions of Gartner's model and for the case of n-type semiconductor, the photocurrent is given by [4],

$$I_{ph} = - q \Phi_o \left(1 - \frac{e^{-\alpha W}}{1 + \alpha L_p} \right) \qquad .....(1)$$

where Φ_o is the photon flux, α is the absorption coefficient, L_p is the hole diffusion length, q is electronic charge and W the width of depletion layer which is given by,

$$W = W_o (V-V_{fb})^{1/2} \qquad .....(2)$$

and

$$W_o = \left(\frac{2 \varepsilon \varepsilon_o}{q N_D} \right)^{1/2} \qquad .....(3)$$

where V_{fb} is flat band potential, $(V-V_{fb})$ is the band bending, ε and ε_o are the dielectric constants of semiconductor and the vacuum respectively and N_D is the donor concentration.

Substituting the value of W in equation (1) and if $L_p << 1$ and $\alpha W_o (V-V_{fb})^{1/2} << 1$, the relation between applied potential and photocurrent becomes,

$$(V-V_{fb}) \simeq \left(\frac{I_{ph}}{\alpha W_o q \Phi_o} \right)^2 \qquad .....(4)$$

This equation is used to estimate the value of flat band potential of the PEC cell. A linear relationship between the square of the photcurrent and voltage applied was observed and is shown in Fig.6.1 for two different wavelengths. The

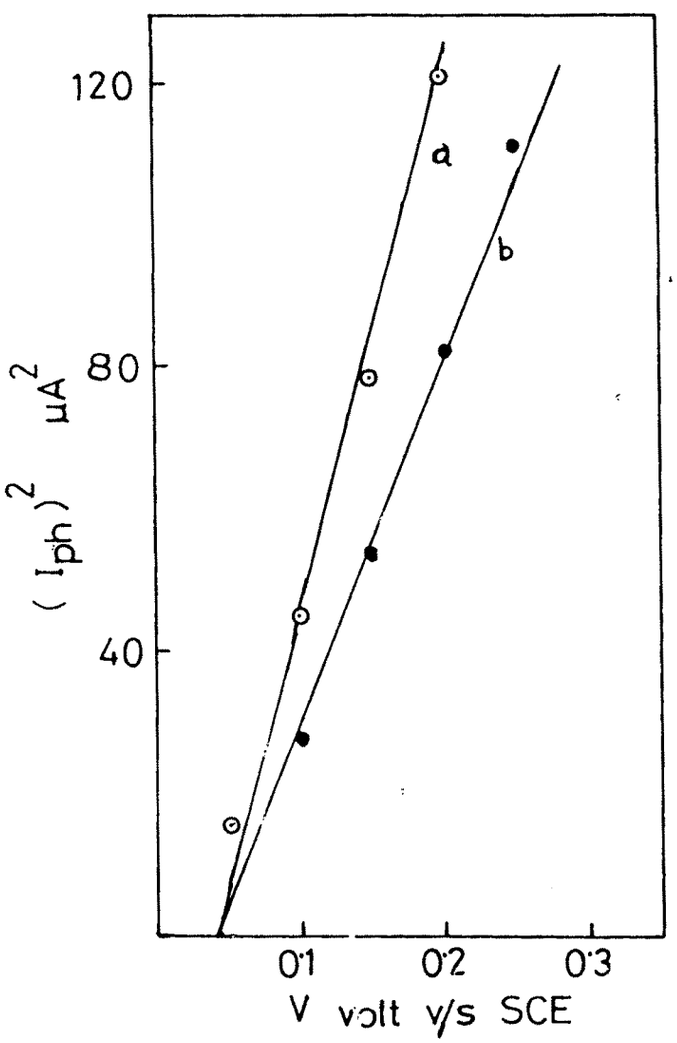

Fig.6.1 : The square of the photocurrent versus applied potential for a WO_3 electrode at (a) 375 nm and (b) 425 nm wavelength of incident light.

value of the flat band potential was obtained by extrapolating the I_{ph}^2 versus V plot to zero photocurrent [13]. The linear plots obtained in Fig.1 yields the V_{fb} of 0.04 V versus SCE for two different incident wavelengths viz. 375 and 425 nm. This value of V_{fb} agrees with in 0.1 V with the value of V_{fb} obtained from Mott-Schottky plots. Similar types of results were obtained by M.A.Butler [4]. He used single crystals of WO_3 grown by vapour transport method and using 1 M sodium acetate as an electrolyte, reported the value of V_{fb} determined from the photoresponse to be 0.1 V versus SCE, agree within 0.2 V with the value obtained by capacitance measurements using a Mott-Schottky plot. The capacitance in PEC cell system depends strongly on sample history and electrolyte. Thus it can be said that, the photoresponse measurements are more reliable than the capacitance technique which is sensitive to surface states and adsorbed species. The difference in the value of V_{fb} obtained, in this case and that obtained by M.A.Butler [4], from photoresponse measurements can be attributed to the difference in nature of samples used.

According to Kennedy and Frese [14], Gartner's theory of the Schottky barrier model to the semiconductor electrolyte interface also provides, within some limitations, a direct determination of donor density and the hole diffusion length. In fact equation (1) leads to equation,

$$\ln (1-\eta') = -\alpha \left(\frac{2\,\varepsilon\varepsilon_o}{q\,N_D}\right)^{1/2} (V-V_{fb})^{\frac{1}{2}} - \ln (1+\alpha L_p) \qquad \ldots\ldots(5)$$

where η' represents the quantum efficiency,

$$\eta' = \frac{I_{ph} . h\nu}{q \Phi_o} = \frac{\text{photocurrent X } h\nu}{q. \text{ Intensity of light}}$$

According to equation (5) plot of $\ln (1-\eta')$ versus $(V - V_{fb})^{1/2}$ should be linear with slope equal to $-\alpha \left(\frac{2 \varepsilon \varepsilon_o}{q.N_D}\right)^{1/2}$ and an intercept of $-\ln (1+ \alpha L_p)$ from which N_D and L_p can be obtained. Fig.2 shows plots of $\ln (1- \eta')$ versus $(V-V_{fb})^{1/2}$ for light of wavelengths 375 and 425 nm. Using the value of $\alpha = 2.13 \times 10^4 \text{ cm}^{-1}$ obtained from optical absorption measurements and $\varepsilon = 50$, the analysis of Fig.6.2 yielded the carrier concentration N_D to be about $6 \times 10^{16} \text{ cm}^{-3}$ and hole diffusion lengths were 0.05 and 0.03 μm for incident wavelength 375 and 425 nm respectively. This value of N_D is one order higher and the values of L_p are one order less than that reported by others [4,15]. This discrepancy in the observed value of L_p may be attributed to the different hole mobility factors.

It has been shown that near the band edge α usually follows the relation [16],

$$\alpha = \frac{A (h\nu - Eg)^n}{h\nu} \qquad \ldots\ldots(6)$$

where A is a constant, Eg is the band gap and n is related to the nature of the fundamental optical transition (n=1/2 for direct transition and n=2 for indirect transition). Assuming hat $\alpha W << 1$ and $\alpha L_p << 1$, conditions generally fulfilled in PEC's photoelectrodes, equation (1) can be written as,

$$\eta' = \alpha (L_p + W) \qquad \ldots\ldots(7)$$

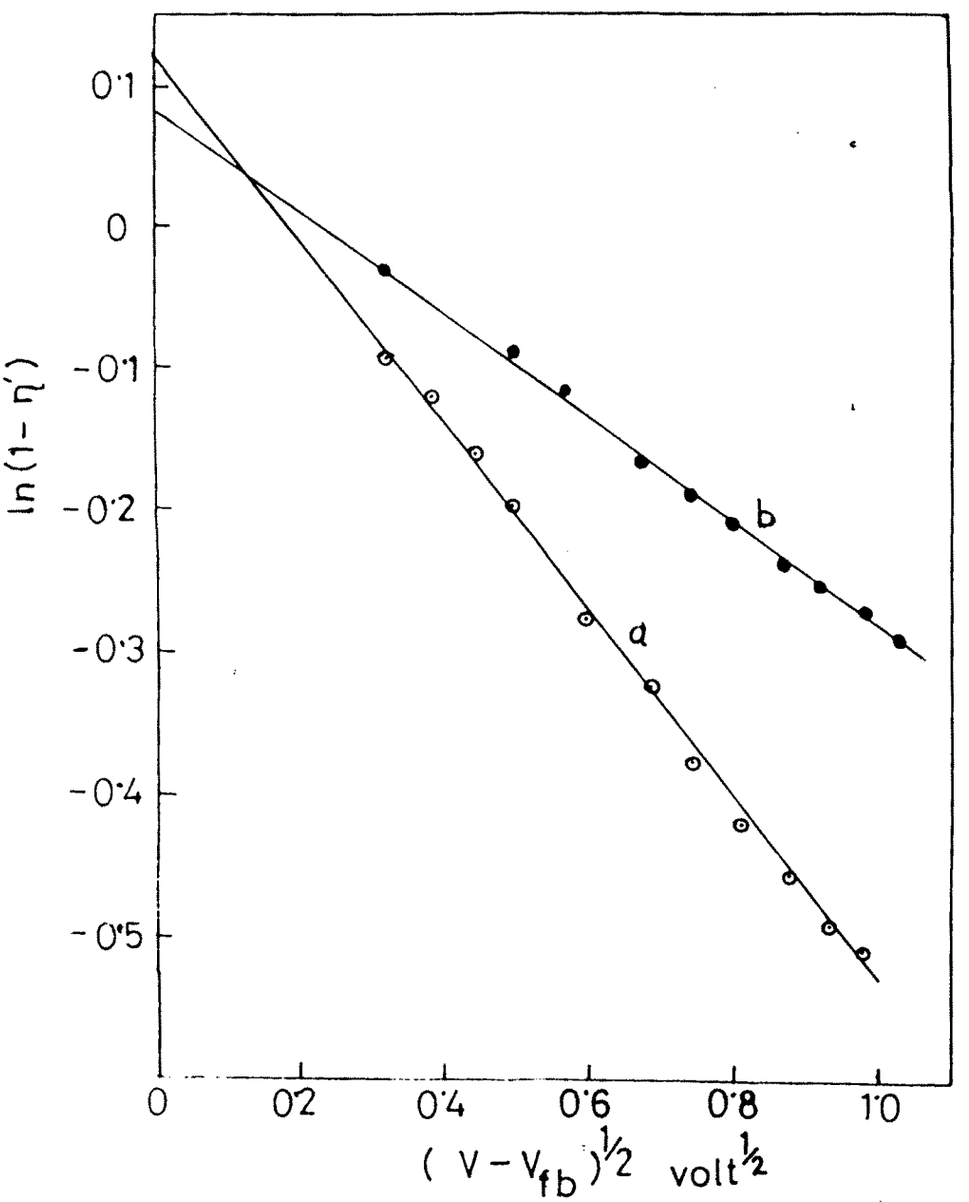

Fig.6.2 : Plot of ln $(1-\eta')$ versus $(V-V_{fb})^{1/2}$ for (a) 375 nm and (b) 425 nm wavelength of incident light.

optical absorption studies for the material showed that the material of film is showing direct optical transition.

From the equation (5) and (6), for the direct band gap semiconductors one obtains,

$$(\eta' h\nu)^2 = (L_p + W)^2 A^2 (h\nu - Eg)$$

Therefore, linear plot of $(\eta' h\nu)^2$ versus $h\nu$ allows Eg to be obtained.

From the survey of literature it is found that the Eg of WO_3 thin film semiconductor varies in the range 2.5 to 3.2 eV depending on sample history and preparation techniques [1-4,6,7].

Fig.6.3 shows the plot of $(\eta' h\nu)^2$ versus $h\nu$ and extrapolation of the linear portion leads to value of 2.9 eV. The value of Eg obtained from optical absorption study was 2.54 eV. For optical absorption study only WO_3 thin film was scanned while in this case WO_3 thin film dipped in Na_2SO_4 electrolyte was used. The difference in the obtained values of bandgap may arise because of the presence of builtin potential across the semiconductor-electrolyte interface.

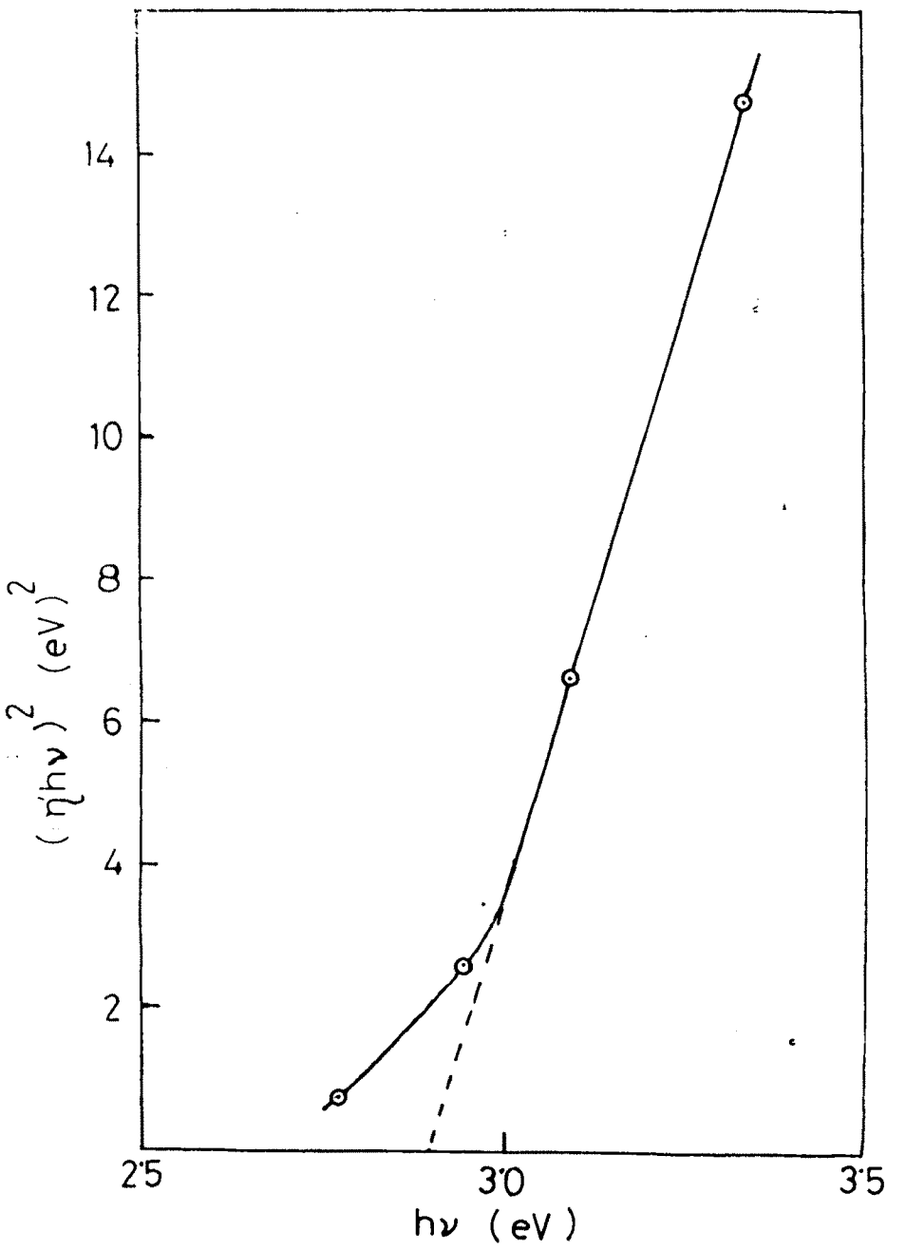

Fig. 6.3 : The plot of variation of quantum efficiency with photon energy for 0.2 volt applied potential to the WO_3 electrodes.

REFERENCES :

[1] K.A.Hardee and A.J.Bard, J.Electrochem. Soc.124(1977)215 .

[2] S.K.Deb,Phil.Mag.27(1973)801.

[3] W.Gissler and R.Memming,J.Electrochem.Soc.124 (1977)1710 .

[4] M.A.Butler,J.Appl.Phys.48 (1977)1914.

[5] M.A.Butler,R.D.Nasby and Rod K.Quinn,Solid State Commun. 19 (1976) 1011.

[6] F.Di Quarto,A Di Paola and C.Sunseri, Electrochem.Acta 26 (1981) 1177.

[7] Martine Spichinger-Ulmann and Jan Augustynski J.Appl. Phys. 54 (1983) 6061.

[8] J.T.Law, in Semiconductors, (Edited by B.Hannay) P.676 Reinhold, New York (1959).

[9] P.Salvador,J.Appl.Phys.55 (1984) 2977.

[10] M.T.Gutierrez and P.Salvador,Solar Energy Materials, 15 (1987)19.

[11] A.Fujishima,K.Honda and S.Kikuchi,J.Chem.soc.Jpn.72(1969) 108.

[12] G.Hodes,D.Cahen and J.Manassen,Nature 260(1976)312.

[13] W.W.Gartner,Phys.Rev.116(1959)84.

[14] Kennedy J.H.,Frese,Jr.K.W.,J.Electrochem.Soc.,23(1976)1683.

[15] A.Fujishima and K.Honda,Nature 238 (1972)37.

[16] A.Aruchamy,G.Aravamudan and G.V.Subba Rao,Bull.Mat.Sci. 4 (1982) 483.