Studies on the photoelectrochemical cell formed with WO_3 photoanode by using Gartner's model

P S PATIL* and P R PATIL

Department of Physics, Shivaji University, Kolhapur 416 004, India

MS received 19 April 1994; revised 9 April 1996

Abstract. WO_3 thin films have been prepared by employing spray pyrolysis technique. Photoelectrochemical (PEC) cell was formed using WO_3 thin film as a photoanode and 0.1 M Na_2SO_4 as an electrolyte. Different physical parameters of the PEC cell such as flat band potential, donor density, hole diffusion length and band gap energy were determined by using Gartner's model.

Keywords. Tungsten trioxide; photoelectrochemical cell; Gartner's model.

1. Introduction

Tungsten oxides are extensively studied materials for their use as photoanodes in photoelectrochemical cells. Literature shows that different values of band gap energy and flat band potential have been reported by different authors (Deb 1973; Butler *et al* 1976; Butler 1977; Gissler and Memming 1977; Hardee and Bard 1977; Quarto *et al* 1981; Ulmann and Augustynski 1983). A large influence on both parameters seems to be due to the different preparation techniques and mixed phase formation of WO_3 . 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 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 (Law 1959). Therefore, it is of interest to estimate these parameters for WO_3 thin films prepared by spray pyrolysis technique.

The parameters such as band gap energy (E_g) of a semiconductor, concentration of carriers (N_D), flat band potential (V_{fb}) could be determined by photoelectrochemical technique (Salvador 1984; Gutierrez and Salvador 1987). 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 (Fujishima *et al* 1969). In this investigation the same model has been used for the determination of different parameters of PEC cell formed with sprayed WO_3 thin film.

2. Experimental

WO_3 thin films were prepared by spraying ammonium tungstate on to fluorine doped tin oxide (FTO) coated glass substrates kept at 250°C and further heated at 550°C in air for 6 h in a furnace. Photoelectrochemical cell was formed using WO_3 film 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 FTO 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 a nanometer and digital DC voltmeter respectively.

3. Results and discussion

WO₃ powder (LR grade, The British Drug House Ltd.) was dissolved in hot ammonia solution thereby forming ammonium tungstate. The chemical reaction is as follows:

The ammonium tungstate solution of 0.04 M concentration was then sprayed onto the fluorine doped tin oxide coated glass substrates maintained at optimized temperature (250°C). The spray rate and deposition time were 25 cc/min and 4 min respectively. The following reaction took place:

Films were further heated at 550°C in air for 6 h in a furnace. The films (1.2 μm thick) were found to be well covered, adherent to the substrate and lemon yellow in colour. XRD studies showed that the films were polycrystalline and consisted of mixed phases of 50% monoclinic and 50% triclinic WO₃ (Patil and Patil 1994).

The PEC cell was fabricated by employing these films as photoanodes and shown in figure 1. The cell configuration was as follows:

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 (Butler 1977),

$$I_{\text{ph}} = -q\phi_0 \left[1 - \frac{\bar{e}^{\alpha w}}{1 + \alpha L_p} \right], \quad (1)$$

Figure 1. Schematic of photoelectrochemical cell. (1. Photoelectrode, 2. counter electrode, 3. SCE and 4. electrolyte).

Figure 2. The square of the photocurrent vs applied potential for a WO_3 electrode at (a) 375 nm and (b) 425 nm wavelengths of incident light. Voltage was measured against a standard calomel electrode.

where ϕ_0 is the photon flux, α the absorption coefficient, L_p the hole diffusion length, q the electronic charge and W the width of depletion layer which is given by

$$W = W_0(V - V_{fb})^{1/2}, \quad (2)$$

and

$$W_0 = \left(\frac{2\epsilon\epsilon_0}{qN_D} \right)^{1/2}, \quad (3)$$

where V_{fb} is flat band potential, $(V - V_{fb})$ is the band bending, ϵ and ϵ_0 are the dielectric constants of semiconductor and the vacuum respectively and N_D is the donor concentration.

Substituting the value of W in (1) and if $L_p \ll 1$ and $\alpha W_0(V - V_{fb})^{1/2} \ll 1$, the relation between applied potential and photocurrent becomes,

$$(V - V_{fb}) \approx \left(\frac{I_{ph}}{\alpha W_0 q \phi_0} \right)^2. \quad (4)$$

This equation is used to estimate the value of flat band potential of the PEC cell. A linear relationship between the square of the photocurrent and applied voltage was observed and is shown in figure 2 for two different wavelengths. The value of

Figure 3. Plot of $\ln(1 - \eta')$ vs $(V - V_{fb})^{1/2}$ for (a) 375 nm and (b) 425 nm wavelengths of incident light.

the flat band potential was obtained by extrapolating the straight lines to zero photocurrent and was equal to 0.04 V (SCE) for 375 and 425 nm incident wavelengths respectively.

According to Kennedy and Frese (1976), Gartner's theory of the Schottky barrier model to the semiconductor electrolyte interface also provides, with some limitations, a direct determination of donor density and the hole diffusion length.

$$\ln(1 - \eta') = - \left(\frac{2\epsilon\epsilon_0}{qN_D} \right)^{1/2} (V - V_{fb})^{1/2} - \ln(1 + \alpha L_p), \quad (5)$$

where η' represents the quantum efficiency,

$$\eta' = \frac{I_{ph} \cdot h\nu}{q\phi_0} = \frac{\text{Photocurrent} \times h\nu}{q \times \text{Intensity of light}}.$$

According to (5) plot of $\ln(1 - \eta')$ vs $(V - V_{fb})^{1/2}$ should be linear with slope equal to $-(2\epsilon\epsilon_0/q \cdot N_D)^{1/2}$ and an intercept of $-\ln(1 + \alpha L_p)$ from which N_D and L_p can be obtained. Figure 3 shows plot of $\ln(1 - \eta')$ vs $(V - V_{fb})^{1/2}$ for light of wavelength 375 and 425 nm. Using the value of $\alpha = 2.13 \times 10^4 \text{ cm}^{-1}$ obtained from optical absorption measurements and $\epsilon = 50$, the analysis of figure 3 yields carrier concentration N_D to be about 6.4×10^{20} and $12.3 \times 10^{20} \text{ cm}^{-3}$ and hole diffusion lengths as 0.05 and 0.03 μm for incident wavelengths 375 and 425 nm respectively. The values of hole diffusion length appear reasonable although, as yet, there are no independent measurements of this quantity.

Figure 4. The plot of variation of quantum efficiency with photon energy for an applied potential of 0.2 V to the WO_3 electrode.

The band gap energy of the material is determined by using the following relation,

$$(\eta' h\nu)^2 = (L_p + W)^2 A^2 (h\nu - E_g), \quad (6)$$

where A is a constant and η' is quantum efficiency. The plot of $(\eta' h\nu)^2$ vs $(h\nu)$ allows E_g to be obtained. Figure 4 shows the variation of $(\eta' h\nu)^2$ vs $(h\nu)$. Extrapolation of linear portion of this curve gives the value of E_g equal to 2.9 eV. This plot suggests that sprayed WO_3 is a direct band gap material. The value of E_g obtained is in agreement with others (Miyake *et al* 1982, 1984).

4. Conclusions

Gartner's model is useful in estimating different physical parameters of the photo-electrode of PEC cell. The value of V_{fb} , determined from the photoresponse is 0.04 V. The values of carrier concentration are 6.4×10^{20} and $12.3 \times 10^{20} \text{ cm}^{-3}$ whereas hole diffusion lengths are 0.05 and 0.03 μm for incident wavelengths 375 and 425 nm respectively. The material shows direct band gap and the value of band gap energy is 2.9 eV.

Acknowledgement

One of the authors (PRP) acknowledges UGC, New Delhi for the grant of a Teacher Fellowship.

References

- Butler M A, Nasby R D and Quinn R K 1976 *Solid State Commun.* **19** 1011
Butler M A 1977 *J. Appl. Phys.* **48** 1914
Deb S K 1973 *Philos. Mag.* **27** 801
Fujishima A, Honda K and Kikuchi S 1969 *J. Chem. Soc. Jpn* **72** 108
Gissler W and Memming R 1977 *J. Electrochem. Soc.* **124** 1710
Gutierrez M T and Salvador P 1987 *Sol. En. Mater.* **15** 19
Hardee K A and Bard A J 1977 *J. Electrochem. Soc.* **124** 215
Kennedy J H and Frese K W 1976 *J. Electrochem. Soc.* **123** 1683
Law J T 1959 in *Semiconductors* (ed.) B Hannay (New York: Reinhold) p. 676
Miyake K, Kaneko H and Teramoto Y 1982 *J. Appl. Phys.* **53** 1511
Miyake K, Kaneko H, Samo M and Suedomi N 1984 *J. Appl. Phys.* **55** 2747
Patil P S and Patil P R 1994 *Tr. J. Phys.* **18** 1
Quarto F Di, Paola A Di and Sunseri C 1981 *Electrochim. Acta* **26** 1177
Salvador P 1984 *J. Appl. Phys.* **55** 2977
Ulmann M S and Augustynski J 1983 *J. Appl. Phys.* **54** 6061