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Semiconducting properties of TiO_2 films thermally formed at 400° C

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Titanium oxide films, TiO_2, were prepared on metallic titanium substrates employing a thermal treatment at 400° C under normal air atmosphere, with various annealing times (15, 25 and 45 min). Cyclic voltammetry and electrochemical impedance spectroscopy techniques were used to study the electrochemical and electrical characteristics of these films. The potential range for the voltammetric measurements was −0.80 to 8.00 V vs MSE (mercurous sulfate reference electrode). An analysis of the capacitance values of these semiconducting oxide films gave information about their electronic characteristics. From Mott–Schottky plots the donor concentration (N_D) and the flat band potential (E_{fb}) were obtained. N_D values ranged from $14 \times 10^{22}\,cm^{-3}$ to $3.3 \times 10^{22}\,cm^{-3}$, while E_{fb} values ranged from −0.40 to −0.98 V vs MSE, depending on the heating times for the oxide growth. The thickness of the space charge region, calculated from the minimum value of the capacitance at high band bending, varied between 1.45 and 2.13 nm.

1. Introduction

Many studies have been reported in the literature on TiO_2 films obtained by electrooxidation of titanium [1–4]. Studies on thermally generated films are rather scarce, particularly those at temperatures below 600° C with short calcination times [5, 6]. These films are interesting because dimensionally stable anodes (DSA®) which use a metallic titanium substrate, are prepared under these low-temperature and time conditions, and are widely used in industrial electrochemical processes [7, 8].

Studies on the semiconducting properties of TiO_2 electrodes have received more attention since the initial studies of the photo-oxidation of water were at single crystals of n-TiO_2 (rutile), used as photoanodes [9]. Such properties depend on various factors including surface pretreatment of the titanium substrate, the preparation technique, the temperature and duration of heating, and the partial pressure of oxygen during the oxidation process [10].

For many years intensive efforts have been made to build low cost solar cells using semiconductor materials immersed in a suitable electrolyte solution. These devices, commonly named photoelectrochemical cells (PEC) carry out the photo-assisted splitting of water processes.

Anodic or thermal oxide films grown on some metals (for example, titanium(IV) oxide on titanium metal) are wide-gap n-type semiconductors, behaviouring just as PEC. The suitability of TiO_2 as anode material in the photoelectrolysis of water resides in its chemical stability to aggressive aqueous solutions and in its lattice stability in the presence of the oxidant photogenerated holes. It has been found that the polycrystalline TiO_2 prepared at high temperatures (500–600° C) show visible light response [11]; these being more suitable for the photoanodes than the single crystals because of cost and ease in the preparation process.

One of the major factors in determining the performance of PEC devices are the physical properties of the semiconductor material, and the modifications produced by different preparation procedures. As the photoresponse is determined by the Schottky-like junction between the semiconductor film and the electrolyte it is very useful to know in some detail those properties as flat-band potentials (that determine the relative Fermi levels of the semiconductor and electrolyte, and therefore the amount of band bending at the interface), density and lifetime of minority carrier, nature of the optical transitions, and so on. On the other hand, the flat-band potentials values obtained from photoresponse experiments are normally comparable with those obtained by capacitance measurements using Mott–Schottky plots.

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The aim of the present work was to better characterize those low-temperature formed titanium oxide films, using cyclic voltammetry and electrochemical impedance spectroscopy techniques to analyse the electrochemical and electrical properties of the TiO_2 films prepared at 400° C. The capacitance of the oxide films is analysed as a function of the applied potential for different heating times of the titanium substrate, and parameters such as donor number (N_D), thickness (δ) and flat-band potentials (E_{fb}) were obtained.

2. Experimental details

Titanium oxide films, TiO_2, were thermally grown on metallic titanium discs 1.2 cm diam. (Koch-Light 99.98%) by heating the discs for various times (15, 25 and 45 min) at 400° C under an atmosphere of air. The electrode surface exposed to the solution in the electrochemical experiments corresponded to one circular face (1.13 cm^2 geometric area), the rest of the surface being covered with a nonconductive paint.

The titanium substrate was mechanically polished with 600 and 1200 grade SiC paper, and then chemically polished with an $HF(48\%)$-$HNO_3(65\%)$-H_2O (1 : 4 : 5 in volume) mixture for 15 s, and finally fully rinsed with purified water in an ultrasonic bath.

The electrochemical measurements were performed in a conventional three electrodes cell with a platinum counter electrode and a $Hg/Hg_2SO_4/Na_2SO_4$ (0.5 M) reference electrode. Unless otherwise indicated, all potentials refer to that of this electrode. The supporting electrolyte was 0.5 M Na_2SO_4 at pH 4.0 prepared from purified and deionized water (Milli RO-Milli Q system from Millipore®). The electrochemical measurements were performed at room temperature (≃ 25° C).

Voltammetric experiments were performed with a Wenking LB 75 potentiostat and a EG&G Parc 175 wave generator, and the current–potential curves were recorded with an XY Omnigraphic 2000 Recorder (Houston Instrument). Electrochemical impedance spectra were recorded using a EG&G Parc 124 A Lock-in amplifier with a Nicolet 206 digital oscilloscope, linked to a computer by an RS-232 interface. The sinusoidal signal applied to the system was generated by a Hewlett Packard 3310B wave generator, with a constant amplitude of 10 mV.

3. Results and discussion

Figure 1 shows cyclic voltammograms recorded with a potential range of −0.80 and 8.00 V at a potential sweep-rate of 0.10 V s^{-1} for an oxide thermally grown at 400° C for 15 min. This figure shows that there is a very small current associated with the passive state of the electrode up to approximately 3.0 V, and above this potential the current increase continuously. This type of response contrasts with that observed at a polished titanium electrode, which shows a constant current plateau corresponding to the formation of an anodic oxide film according to the reaction [1, 2, 12]

$$Ti + 2H_2O \longrightarrow TiO_2 + 4H^+ + 4e^- \qquad (1)$$

Titanium is a typical valve metal and its potentiodynamic response shows an anodic current that reaches an almost steady value during the first anodic potential sweep, according to the high-field mechanism for oxide film growth [13, 14]. The anodic current increases at potentials higher than 3.0 V due to simultaneous oxygen evolution. On the other hand, thermally formed films exhibit much higher currents above 3.0 V than those observed on electrochemically formed TiO_2 films [1, 2], although such currents also corresponds to oxygen evolution. However, the total anodic current decreases significantly after successive potential-sweep cycles due to formation of a thicker and more aged oxide film on the electrode.

To determine the electrical properties of the TiO_2 oxides, impedance measurements were performed between −0.65 and 0.05 V. This potential range corresponds to the region of Mott–Schottky-type behaviour for these oxides. The frequency range was between 10 Hz and 3 kHz. Figure 2 shows Bode plots, i.e. the variation of the total impedance (log Z, open circles) and the phase angle (ϕ, dark

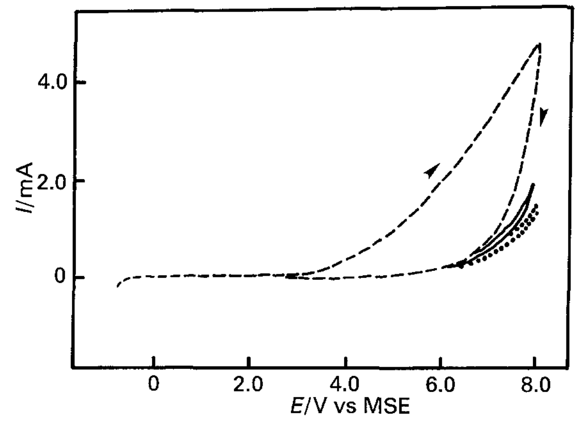

Fig. 1. First three cyclic voltammograms of titanium electrode previously heated at 400° C for 15 min. Sweep rate: 0.10 V s^{-1}. Electrolyte: 0.5 M Na_2SO_4, pH 4.0. Key: (— — —) 1st scan; (———) 2nd scan; (· · · ·) 3rd scan.

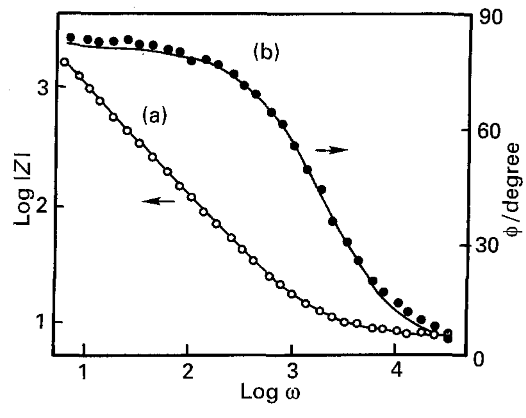

Fig. 2. Plot of log Z against log ω (curve (a)) and of the phase angle (ϕ) against log ω (curve (b)). (○) Experimental data, (———) best fit to an RQ series circuit, for TiO_2 grown at 400° C for 45 min. Z is given in ohms and ω in hertz.

circles) as a logarithmic function of the frequency (logω, where $\omega = 2\pi f$). No equivalent *RC* series circuit gave a good fit for the behaviour of this system. The equivalent circuit giving a better fit was an *RQ* series circuit, where *Q* is a constant phase angle element. The impedance of the system can then expressed empirically as

$$Z = R + \frac{Q}{(\mathrm{i}\omega)^{1-\alpha}} \tag{2}$$

where *Q*, which represents the constant-phase element, has the dimensions of $\Omega\,\mathrm{cm}^2\,\mathrm{s}^{-(1-\alpha)}$, and α is a dimensionless parameter having a value between zero and unity [14]. The best fit obtained with the *RQ* equivalent circuit is shown in Fig. 2 (for a TiO_2 film formed by 45 min of heating) and corresponds to $R = 7.41\,\Omega$, $Q = 2.23 \times 10^{-5}\,\Omega\,\mathrm{cm}^2\,\mathrm{s}^{-(1-\alpha)}$, and $\alpha = 0.93$.

The formula for a combination of capacitors in series can be applied to the TiO_2/electrolyte system according to

$$C_\mathrm{m}^{-1} = C_\mathrm{H}^{-1} + C_\mathrm{sc}^{-1} \tag{3}$$

where C_m is the experimental capacity, C_H the capacity of the Helmholtz layer at the oxide-electrolyte interface and C_sc is the capacity of the space-charge region in the oxide film.

The capacitance values (C_m) obtained assuming an series *RQ* circuit were corrected by the Helmholtz layer capacitance according to Equation 3 assuming a $20\,\mu\mathrm{F\,cm}^{-2}$ value for C_H. The C_sc values were then subjected to analysis using the Mott–Schottky equation [15] which correlates the capacity of the space-charge region of a semiconductor (C_sc) with the applied potential (*E*):

$$\frac{1}{C_\mathrm{sc}^2} = \frac{2}{\epsilon\epsilon_0 q N_\mathrm{D}}\left\{E - E_\mathrm{fb} - \frac{kT}{q}\right\} \tag{4}$$

where N_D is the donor concentration for an *n*-type semiconductor, E_fb is the flat band potential, ϵ is the relative permittivity of the oxide, and ϵ_0 is the vacuum permittivity. It can be demonstrated that N_D and E_fb can be obtained from the slope and the intercept of an $1/C_\mathrm{sc}^2$ against *E* (Mott–Schottky) plot, respectively. Figures 3, 4 and 5 show such Mott–Schottky plots for films formed during heating periods of 15, 25 and 45 min, respectively. For all cases, a strong dispersion of the data arises with frequency. Similar results have been reported for passive films on stainless steel [16]. In spite of the frequency dispersion, it is still possible to obtain significant values for the semiconducting properties based on models proposed for different responses.

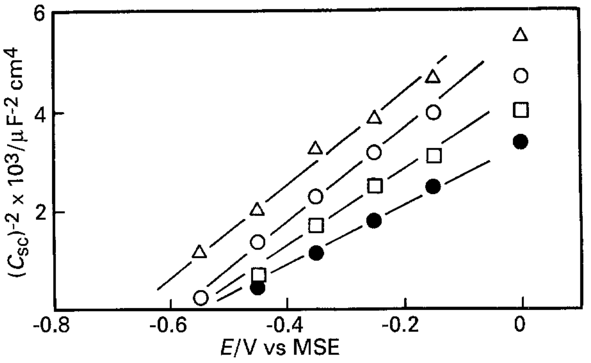

Fig. 4. Mott–Schottky plot for an oxide film obtained by heating titanium at 400° C for 25 min. Frequency: (△) 1000, (○) 320, (□) 80 and (●) 20 Hz.

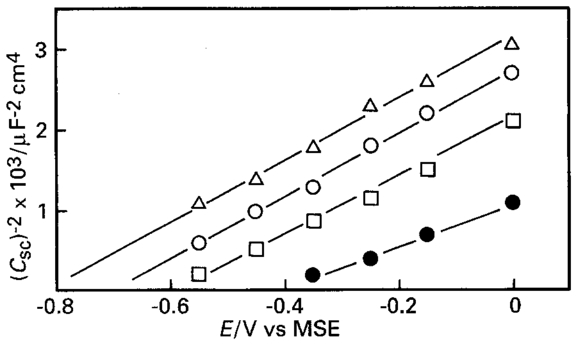

Fig. 3. Mott–Schottky plot for an oxide film obtained by heating titanium at 400° C for 15 min. Frequency: (△) 1000 (○) 320, (□) 80 and (●) 20 Hz.

Dutoit *et al.* [16] have distinguished two diverse types of behaviour which are referred to as 'A-type' and 'B-type', respectively. For 'A-type' behaviour, the Mott–Schottky plots at all frequencies are nearly parallel (equivalent to the ones in Fig. 3) and the intercepts on the *E*-axis is shifted toward more negative potentials with increasing frequency. This type of behaviour permits N_D to be determined but not E_fb. For 'B-type' behaviour, the Mott–Schottky plots converge to a common point on the potential axis (Fig. 5), i.e. to a common flat band potential. However, it is not possible to determine just one N_D value. Recently, Di Paolo [17] has distinguished a third case, which was called '(A + B)-type' behaviour, where the slopes of the Mott–Schottky plots, as well as their intercepts on the potential axis, are frequency dependent; therefore they yield no information about E_fb or N_D. The Mott–Schottky plots converge to a common value at low frequencies (generally below 300 Hz) but become nearly parallel at higher frequencies.

Oxides obtained by heating Ti for 15 min show parallel Mott–Schottky plots for different frequencies (A-type behaviour) whereas those prepared by heating for 45 min intercept at a common value

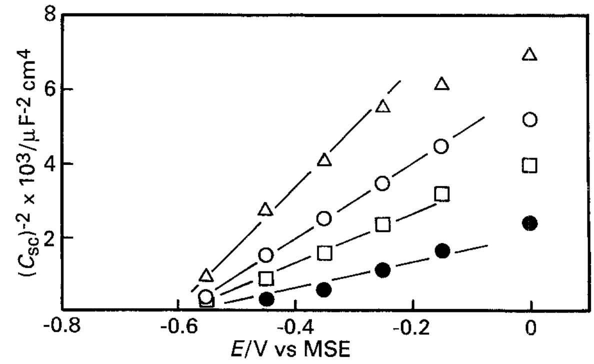

Fig. 5. Mott–Schottky plot for an oxide film obtained by heating titanium at 400° C for 45 min. Frequency: (△) 1000 (○) 320, (□) 80 and (●) 20 Hz.

on the potential axis (B-type behaviour). An (A + B)-type behaviour is exhibited by oxides obtained by heating for 25 min.

This frequency dispersion behaviour is usually explained [16–18] in terms of the following: (a) a non-uniform distribution of donors; (b) the contribution of surface states to the capacity response; (c) a dielectric relaxation phenomenon; (d) the amorphous nature of the film, and (e) the presence of extra donor states.

To compare our results with those reported in the literature [2] for anodically grown TiO_2 films, N_D and E_{fb} values were calculated from the capacity measurements obtained at 1 kHz frequency, using a value of 40 for the oxide dielectric constant. This dielectric constant value is similar to those for other thermal oxide films, and is a reasonable value considering the fact that thermally grown TiO_2 is an oxide in a highly dehydrated state [19]. As discussed above, the flat-band potential is independent of frequency only for oxides prepared with heating times above 45 min. The thickness of the space-charge region could be estimated in the range where the capacity became essentially independent of the potential. At this stage the thickness of the space-charge region may coincide with the oxide thickness, $\delta = \epsilon\epsilon_0/C$. The calculated parameters obtained at 1 kHz are shown in Table 1. For TiO_2 films grown potentiodynamically up to 1.0 V ($\delta = 3.9$ nm), the reported E_{fb} was of −0.64 V vs SCE while the donor concentration was $1.46 \times 10^{20}\,\mathrm{cm}^{-3}$ [2]. The assumed values for the oxide dielectric constant varied between 50 and 86 taking account of the very high degree of hydration. This assumption, added to the fact that the thickness and doping (due to the preparation technique) are different from those of our thermally grown films, could explain the lower values found for N_D compared with ours.

To focus the differences in the Mott–Schottky behaviour, we have analysed the results corresponding to the frequency range 20 to 1000 Hz. Table 2 shows the dispersion of the E_{fb} and N_D values, which illustrates the behaviour discussed earlier.

The dispersion in the values of the flat-band potentials in Table 2 for oxides grown for 15 min shows that it is not possible to determine accurate E_{fb} values for this particular oxide. This is consistent with the 'type A' behaviour proposed for this oxide. The same can be said for the 'type B' behaviour for oxides grown for 45 min, for which, in this case, the dispersion of the values of N_D increase and the values of E_{fb} decrease. Finally, the extremely high N_D values can be understood as a result of very thin and highly defective oxide films being thermally grown at 400° C, which should be expected to provide large photocurrents. Indeed previous results on TiO_2 films thermally grown at 500–600° C, which are thicker than the ones reported here, have shown photocurrent values of about $1\,\mathrm{mA\,cm}^{-2}$ [10]. Moreover, high values for donor density ($\simeq 10^{21}\,\mathrm{cm}^{-3}$) were also found for 54 nm thick anodic WO_3 films [20]. However, for tungsten oxide films, the authors observed a noticeable influence of the film thickness on the donor concentration in the films due to a sharp decrease in N_D with increasing thickness. Therefore, our results reinforce the well-known influence of the preparation method on the electrical properties of oxide films.

Table 1. Parameters derived from Mott–Schottky plots at 1 kHz for TiO_2 thermally grown for various times at 400° C

t/min	*E_{fb}/V vs MSE*	*$N_D/10^{22}\,cm^{-3}$*	*δ/nm*
15	−0.86	7.0	2.9
25	−0.66	4.0	3.6
45	−0.60	1.6	4.2

Table 2. Parameters derived from Mott–Schottky plots over a frequency range (20 to 1000 Hz) for thermally formed TiO_2 films grown for various times at 400° C

t/min	*E_{fb}/V vs MSE*	*$N_D/10^{22}\,cm^{-3}$*	*δ/nm*
15	−0.45 to −0.86	7.1 to 7.0	2.9
25	−0.54 to −0.66	4.0 to 6.0	3.6
45	−0.55 to −0.60	1.6 to 2.8	4.2

4. Conclusions

The cyclic voltammograms of thermally grown oxide films on metallic titanium substrates at 400° C suggest the formation of very thin TiO_2 films. The thickness of these films should be equivalent to those of anodic TiO_2 films potentiodynamically grown up to 2 to 3 V, according to the results in Fig. 1. These low-thickness values are in agreement with previous work on TiO_2 films grown at other temperatures [10] and indicate that the assumptions made for their determination are reasonable.

The impedance results show that the concentration of donor species decreases with the increase of the heating time (or the thickness of the film) and the flat-band potential shifts to less negative values. The decrease of N_D with the heating time can be envisaged as due to a more organized lattice structure (less defects) for thicker oxides grown longer at 400° C. The preparation time, therefore, should be taken into account if these materials are to be used as dimensionally stable anodes or photoanodes, since the time factor changes their electrical properties.

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References

[1] O. R. Cámara, C. P. De Pauli and M. C. Giordano, *Electrochim. Acta* **29** (1984) 1111.

[2] R. M. Torresi, O. R. Cámara, C. P. De Pauli and M. C. Giordano, *ibid.* **32** (1987) 1291.

[3] J.-L. Delplancke and R. Winand, *ibid.* **33** (1988) 1539.

[4] *Idem, ibid.* **33** (1988) 1551.

[5] T. Smith, *Surf. Sci.* **38** (1973) 292.

[6] Y.-K. Choi, S.-S. Seo and K.-H. Chjo, *J. Electrochem. Soc.* **139** (1992) 1803.

[7] D. L. Caldwell in J. O'M. Bockris, B. E. Conway, E. Yeager and R. E. White (Eds), 'Comprehensive Treatise of Electrochemistry', vol. 2, Plenum Press, New York (1981) Ch. 2.

[8] D. M. Novak, B. V. Tilak and B. E. Conway, *in* 'Modern Aspects of Electrochemistry' (edited by J. O'M. Bockris, B. E. Conway and R. E. White), vol. 14. Plenum Press, New York (1982) p. 195.

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

[10] K. J. Hartig, J. Lichtscheidl and N. Getoff, *Z. Naturforsch* **36a** (1981) 51.

[11] Y. Matsumoto, J. Kurimoto, J. Amagasaki and E. Sato, *J. Electrochem. Soc.* **127** (1980) 2148.

[12] M. E. Sibert, *ibid.* **110** (1963) 65.

[13] L. Young, 'Anodic Oxide Films', Academic Press, London (1961).

[14] G. C. Wood and S. W. Khoo, *J. Appl. Electrochem.* **1** (1971) 189.

[15] M. E. Dean and U. Stimming, *J. Electroanal. Chem.* **228** (1987) 135.

[16] E. C. Dutoit, R. L. Van Meirhaeghe, F. Cardon and W. P. Gomes, *Ber. Bunsenges Phys. Chem.* **79** (1975) 1206.

[17] A. Di Paola, *Electrochim. Acta* **34** (1989) 203.

[18] F. Di Quarto, C. Sunseri and S. Piazza, *Ber. Bunsenges Phys. Chem.* **90** (1986) 549.

[19] D. R. Lide (Ed), 'Handbook of Chemistry and Physics', CRC 71st edn. Cleveland (1990).

[20] F. Di Quarto, V. O. Aimiuwu, S. Piazza and C. Sunseri, *Electrochim. Acta* **36** (1991) 1817.