Dielectric and structural characteristics of Ta$_2$O$_5$ anodic films formed in phosphoric acid electrolytes

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The duplex nature of Ta$_2$O$_5$ films formed in H$_3$PO$_4$ electrolytes with different concentrations has been characterized by net weight gain measurements of the films during the anodic oxidation, as well as by capacitance and etch-rate measurements of the oxide films. The density and permittivity of each layer of the films formed in different concentrations of the electrolyte have been calculated.

1. Introduction

Owing to their outstanding dielectric characteristics, anodic Ta$_2$O$_5$ films are widely used in electronic devices, such as electrolytic capacitors, MOS transistors, solar cells, etc. [1]. The Ta$_2$O$_5$ anodic films have a very uniform thickness, proportional to the anodization voltage, a high permittivity ($\varepsilon \sim 27$) and are able to withstand field strengths in the range of the anodization electric field, i.e. about $6.5 \times 10^6\,\mathrm{V\,cm^{-1}}$. However, the composition of the anodic Ta$_2$O$_5$ films is not entirely stoichiometric, as a consequence of electrolyte incorporation during the film growth. Depending on the nature and the concentration of the electrolyte, appreciable amounts of electrolyte species are known to incorporate in the external layers of the films, modifying the physicochemical properties of the oxide [2].

Several authors have studied the influence of the electrolyte incorporation on the dielectric characteristics of the films [2, 3]. However, at present, no systematic studies have been carried out in order to assess the effect of the concentration of the anodization electrolyte on the oxide properties. In this paper we report the results of dielectric measurements on Ta$_2$O$_5$ anodic films grown in H$_3$PO$_4$ electrolytes at different concentrations. The results have been correlated with the calculated values of the film density. These values have been obtained by measuring the weight gain during the anodization process. In addition, chemical etch-rate measurements in a buffered solution of hydrofluoric acid have been used to differentiate the duplex nature of these films.

2. Experimental procedure

Tantalum foil of 99.96% purity, supplied by Reframet Hoboken, Belgium was degreased and chemically polished according to standard treatments [4]. Anodic Ta$_2$O$_5$ films were grown in phosphoric acid electrolytes at different concentrations in water. The anodization process was carried out at a constant current density of $0.850\,\mathrm{mA\,cm^{-2}}$ up to a definite voltage. The temperature of the anodization cell was kept constant at $20.0 \pm 0.2°\,\mathrm{C}$ by means of a thermostatic bath. The net weight gain of the sample after anodization was measured with a Mettler balance, Model M3, having a sensitivity of $1.0\,\mu\mathrm{g}$.

After anodizing, chemical dissolution of the Ta$_2$O$_5$ layers was performed in an NH$_4$F/FH solution (40 g per 100 ml) by dipping the samples during successive intervals of 30 sec. Following the immersion, the samples were thoroughly washed in deionized water, and then the capacitance and the loss angle at 100 Hz were measured with an LCR meter, Hewlett–Packard HP Model 4274, using an electrolytic cell with a 10% H$_3$PO$_4$ solution in water.

In some samples surface analysis was also carried out by the ESCA (X-ray photoelectron spectroscopy, XPS) technique, using the $K\alpha$ line of a magnesium lamp ($h\nu = 1253.6\,\mathrm{eV}$) and a semispherical analyser, Leybold–Heraeus, LH-30.

3. Results

During the anodization process at a constant current density the voltage increases almost linearly with time until scintillation or breakdown occurs [5]. As a consequence of the oxide growth, the net weight gain of the samples should be a linear function of the anodization voltage. Fig. 1 shows this behaviour for samples anodized in H$_3$PO$_4$ electrolytes of different concentrations up to the breakdown voltage (marked with an arrow on the upper end of the curves). It is observed that the slope of the curves gets smaller as the concentration of the anodizing electrolyte increases.

The etch-rate characteristics are shown in Fig. 2 for samples anodized at 50, 100 and 150 V in the 0.1 M H$_3$PO$_4$ electrolyte. As can be appreciated the inverse of the capacitance, which is a figure proportional to the oxide thickness, decreases linearly with the dissolution time. The curves display two well-differentiated regions which are attributed to the duplex nature of these films, i.e. an outer layer doped with the electrolyte species and the innermost corresponding to pure stoichiometric oxide [2]. The close parallelism of the
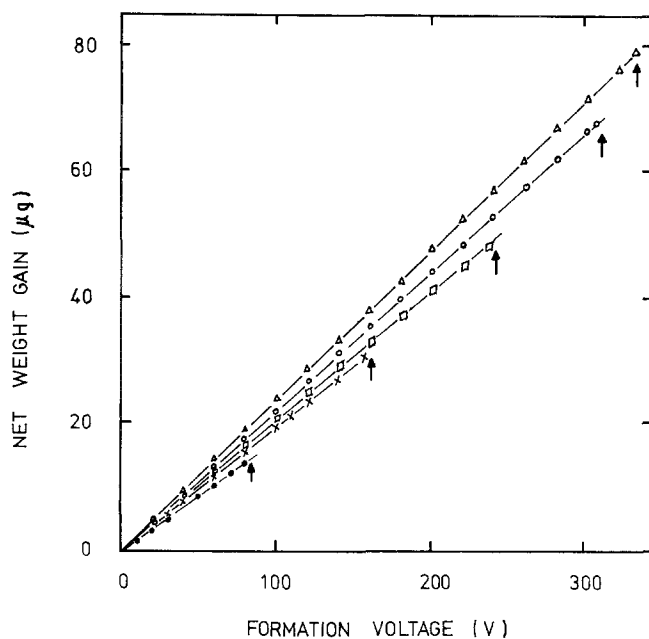
Figure 1 Net weight gain as a function of the anodization voltage for samples anodized in H_3PO_4 electrolytes with different concentrations (the arrows indicate the breakdown voltage): ($\triangle$) 1.0×10^{-3} M, (O) 1.0×10^{-2} M, ($\square$) 2.0×10^{-1} M, ($\times$) 1.0 M, ($\bullet$) 7.4 M.

curves of Fig. 2 indicates the absence of a thickness effect on the oxide etch-rate.

The influence of the concentration of the anodization electrolyte on the etch rate is illustrated in Fig. 3, which shows the inverse of the capacitance as a function of the dissolution time for samples anodized at 50 V. The upper parts of the dissolution curves display increasing etch-rates as the molar concentration of the electrolyte increases. On the contrary, in the lower part of the curves, corresponding to the inner oxide layers, a constant etch rate is observed. Assuming for this layer the permittivity of pure Ta_2O_5, $\varepsilon_2 = 27.6$ [6], the resulting etch rate is on the average $v_2 = 6.084$ nm min^{-1} with a dispersion less than ± 0.2 nm min^{-1}.

Identification of the incorporated species has been carried out by ESCA analysis. Fig. 4 shows typical energy spectra, in the region 1100 to 1130 eV, of a sample anodized at 50 V, obtained before the etching process (Curve 1) and after a dissolution time when the inner layers are reached (Curve 2). The peak appearing in the vicinity of 1120 eV corresponds to the 2p electrons of the phosphorous atoms, which are likely to be incorporated as phosphate ions [7] in the outer oxide layers. The absence of this peak in the inner layers is clearly evident from the results of Fig. 4.
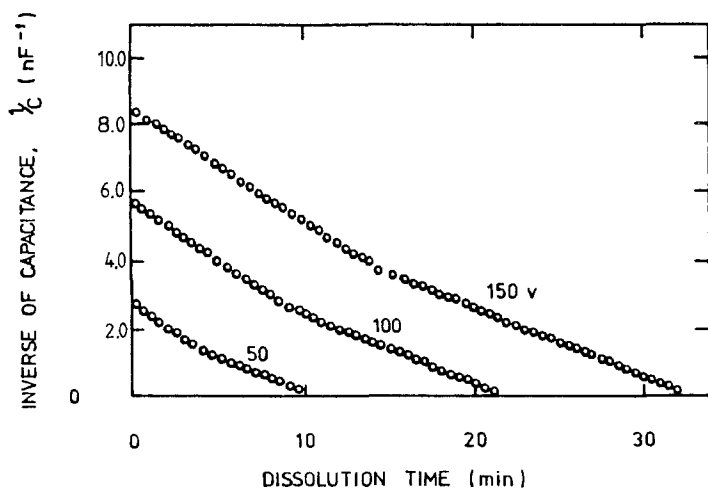
4. Discussion

As it can be appreciated from the above section, the incorporation of the electrolyte species during the anodization process plays an important role in determining the structural and dielectric properties of anodic Ta_2O_5 films. In this regard, it is known that increasing electrolyte concentrations give rise to higher incorporation rates and consequently higher anodization fields, i.e. smaller oxide thickness for a given anodization voltage [1]. In the case of phosphoric acid, the incorporated species (presumably phosphate ions) are located in the outer layers of the film, the inner layers remaining practically unchanged. A decrease of the density and an increase of the relative thickness of the outer layer with the electrolyte concentration have been reported in previous papers [3, 8].

From the net weight gain measurements (Fig. 1), the variation of the mean oxide density, ϱ, with the electrolyte concentration can be calculated through the equation relating the total oxide mass deposited per unit area, Δm_{ox}, with the anodization voltage, ΔV:

$$\Delta m_{ox} = \varrho \frac{\Delta V}{E} \qquad (1)$$

where E is the anodization electric field. For Ta_2O_5, the net weight gain per unit area, Δm_{obs}, can be related
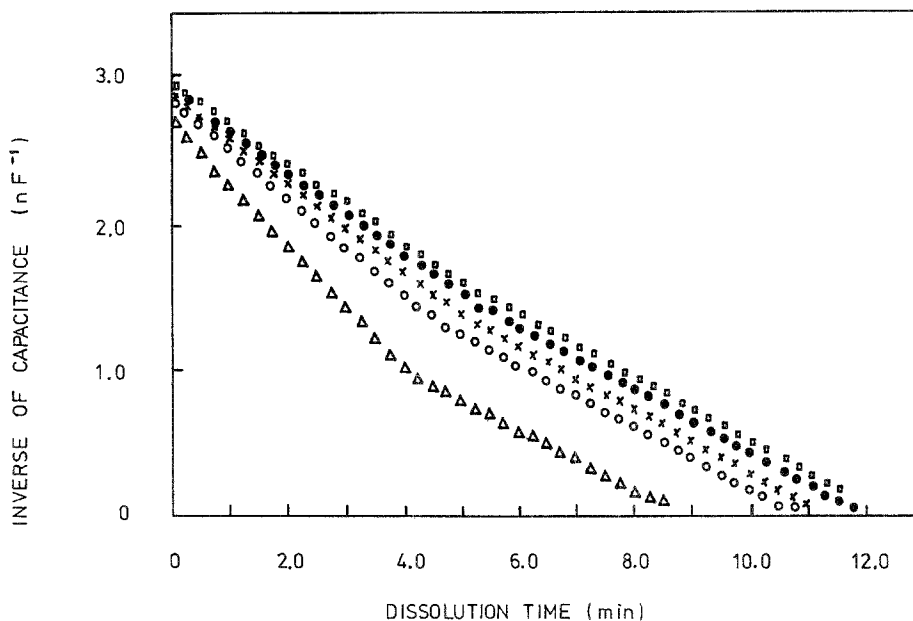

Figure 2 Inverse of the capacitance as a function of the dissolution time for three samples anodized in a 0.1 M H_3PO_4 electrolyte at 50, 100 and 150 V.

Figure 3 Inverse of the capacitance as a function of the dissolution time for samples anodized at 50 V in H_3PO_4 electrolytes with different concentrations: ($\square$) 1.0×10^{-3} M, ($\bullet$) 1.0×10^{-2} M, ($\times$) 2.0×10^{-1} M, ($\circ$) 1.0 M, ($\triangle$) 7.4 M.

to the deposited oxide mass by the equation [9]

$$\Delta m_{ox} = 5.524 f(\gamma) \Delta m_{obs} \qquad (2)$$

In the above formula, provision has been made for a corrective term, $f(\gamma)$, with $f(\gamma) \lesssim 1$, which accounts for the weight of the incorporated species. The constant γ measures the electrolyte incorporation and is defined by the ratio of the current transported by the electrolyte species to the oxidation current [5]. In the Appendix we make the calculation of the corrective term, $f(\gamma)$, on the basis that the incorporated species are phosphate ions, since according to Amsel *et al.* [7] this is the most probable form of incorporation.

Equations 1 and 2 have been used to calculate the mean oxide density, ϱ, as well as the density of the outer layer, ϱ_2, assuming that the film is composed of two homogeneous layers (Fig. 5), with thicknesses x_1 and x_2 given below. For the inner layer, being nearly

pure stoichiometric Ta_2O_5, a density $\varrho_1 = 8.00\,\mathrm{g\,cm}^{-3}$ has been used for all the samples [9]. The results for ϱ and ϱ_2 are given in Table I, along with the parameters E and γ obtained in previous work [5].

Simple arguments can help to explain the decrease of the outer layer density observed in Table I. As stated above, the electrolyte is likely to be incorporated as phosphate anions. In addition, compared to the Ta_2O_5 molecule, the phosphate molecule contains a larger number of ions (four times larger) while its molecular weight is only about twice. Thus, it seems reasonable to expect a lower density for the films formed in the more highly concentrated electrolytes.

The anodization electric field, E, given in Table I has been used to calculate the total oxide thickness, x. Also, we have estimated the thickness of the phosphorus-free region, x_1, as well as the permittivity, ε_2, of the outer layer, from the capacitance values given in
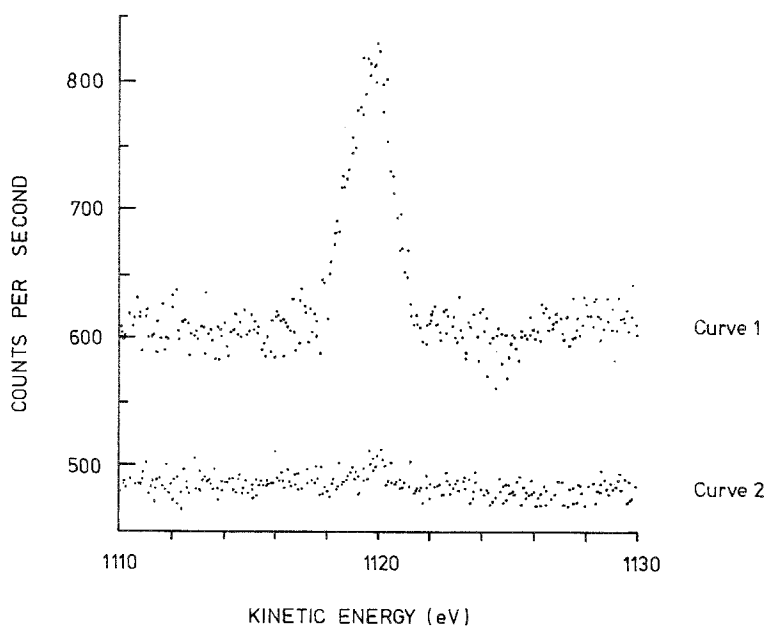

Figure 4 X-ray photoelectron spectra of a sample anodized in a 7.4 M H_3PO_4 electrolyte at 50 V (Curve 1) and the same sample after 5 min dissolution in an HF buffered solution (Curve 2).

TABLE I Effect of the H_3PO_4 concentration, C, on some oxide parameters

C (M)	E (MV cm^{-1})*	γ*	$\Delta m_{obs}/\Delta V$ (g cm^{-2} V^{-1})	ϱ (g cm^{-3})	ϱ_2 (g cm^{-3})†
1.0×10^{-3}	6.25	0.010	0.240	7.90	7.78
1.0×10^{-2}	6.50	0.017	0.225	7.76	7.46
2.0×10^{-1}	6.85	0.030	0.214	7.56	7.04
1.0	6.96	0.050	0.201	7.07	6.02
7.4	7.70‡	0.090§	0.180	6.42	5.41

*From Albella et al. [5].
†Assuming $\varrho_1 = 8.00 \text{ g cm}^{-3}$ [9].
‡From Palacio [12].
§ Extrapolated.

TABLE II Effect of the H_3PO_4 concentration, C, on the etch rate and the permittivity*

C (M)	x_1 (nm)	x_1/x	v_2 (nm min^{-1})	ε	ε_2
1.0×10^{-3}	44.0	0.550	6.84	25.9	24.6
1.0×10^{-2}	42.3	0.550	6.89	25.2	23.3
2.0×10^{-1}	39.4	0.540	6.98	24.5	22.1
1.0	38.4	0.535	7.44	23.6	20.7
7.4	27.3	0.421	9.19	23.0	20.8

*Assuming $\varepsilon_1 = 27.6$ [6].

Fig. 3. For this purpose a two-layer capacitor model has been assumed, the permittivity of the inner layer being $\varepsilon_1 = 27.6$, i.e. that of pure Ta_2O_5 [6].

In Table II we summarize the results obtained for all these parameters. Also reported in Table II are the value of the etch rate of the outer layer, $v_2 = dx_2/dt$, calculated from the corresponding slopes of the curves of Fig. 3.

Table II shows the expected decrease in the permittivity of the outer layer as well as the increase in the etch rate with the increase of the concentration of the anodizing electrolyte. There is also a decrease in the relative thickness of the inner layer. All these characteristics are undoubtedly associated with the variation of the density of the outer layer, as shown in Table I. The variation of the etch rate with the concentration of the phosphoric acid electrolyte has been subjected to some debate, the presence of phosphorus being supposed to inhibit the dissolution of the films [10]. The results obtained in this work do not support this view, although simple calculations demonstrate a slight tendency of the mass dissolution rate to decrease with the concentration of the anodizing electrolyte.

The influence of phosphorus incorporation on the permittivity of the films is also apparent from the results given in Table II. This influence comes probably as a consequence of the variation of the oxide density, as predicted by the Clausius–Mosotti equation. Fig. 6 shows both the calculated values of the oxide density and the permittivity of the outer layer as a function of the concentration of the electrolyte. Also reported in this figure are the results given by Randall [3] for ε_2, which are in good agreement with those obtained in this work. The close correlation shown by the values of ε_2 and ϱ_2 supports the above hypothesis. In fact, the increase of the relative thickness of the outer layer, x_2/x, could be a consequence of the decrease of the density of this layer, as well. In this regard, it is worthwhile to point out that the transport numbers for the cationic and anionic species, very often taken as the relative fractions x_2/x and x_1/x, should be corrected in order to take into account the density changes of each layer.

The phosphorus incorporation in the outer layer has been demonstrated by the ESCA analysis. Surface analysis of samples anodized in the 7.4 M H_3PO_4 electrolyte and subjected to dissolution times shorter than the time needed to reach the inner layer display a phosphorus signal of constant amplitude, as shown in Fig. 4, Curve 1. However, the amplitude decreases by a factor of about ten as soon as the interface between both layers is reached. The phosphorus peak appears at 133.9 ± 0.1 eV binding energy, in close agreement with the results found by Jouve et al. [11] for samples of anodic Nb_2O_5 films grown in phosphoric acid electrolytes. The position of this peak is attributed by these authors to the presence of a phosphate compound. More detailed analyses are now under way in order to determine the stoichiometry of the oxide films and the true nature of the incorporated species.

ORIGINAL Ta SURFACE

$Ta_2 O_5$

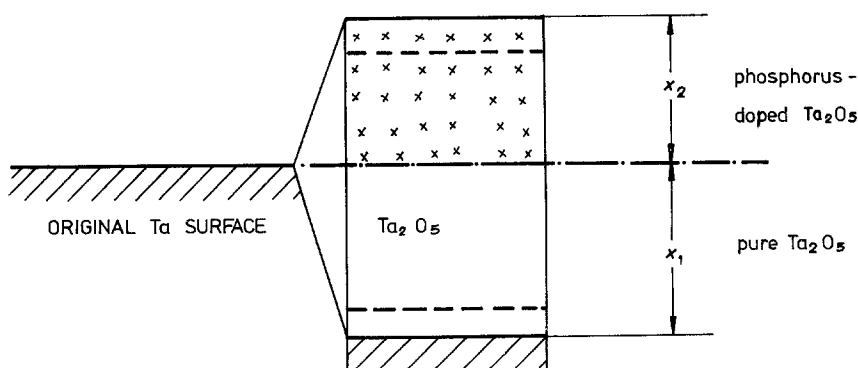x_2 phosphorus - doped Ta_2O_5

x_1 pure Ta_2O_5

Figure 5 Diagram showing the duplex nature of the film. Crosses indicate phosphorus doping of the outer layer (assumed immobile once incorporated into the film). Dashed lines correspond to the thickness obtained in a more concentrated electrolyte.
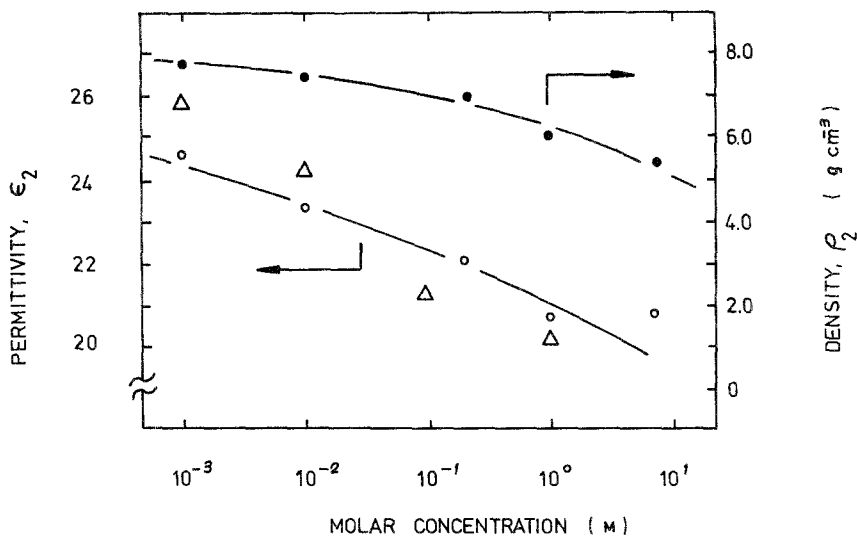
Figure 6 Permittivity, ε_2, and density, ϱ_2, of the outer layer of the Ta_2O_5 films as a function of the molar concentration of the anodization electrolyte.

Appendix

For the reaction $5O^{2-} + 2Ta^{5+} \rightarrow Ta_2O_5$ the observed net weight gain per unit area, Δm_{obs}, is related to the total oxide mass per unit area, Δm_{ox}, through the equation [9]

$$\Delta m_{ox} = 5.524 \Delta m_{obs} \qquad (A1)$$

Similarly, the phosphorus incorporation as phosphate anion will give rise to the reaction (assuming that no other species are present)

$$5O^{2-} + 2Ta^{5+} + \chi(5PO_4^{3-} + 3Ta^{5+})$$

$$\rightarrow Ta_2O_5 \cdot \chi[(PO_4)_5Ta_3]$$
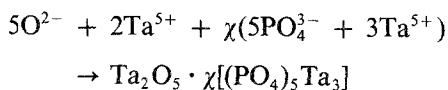
In this case, the corresponding equation is

$$\Delta m_{ox} = 5.524 \left(\frac{1 + 2.303\chi}{1 + 5.396\chi} \right) \Delta m_{obs} \qquad (A2)$$

According to a previous paper [5], γ can be defined as the ratio of the current transported by the electrolyte species, j_2, to the oxidation current, j_1, i.e. $\gamma = j_2/j_1$, then $\chi = 2/3\gamma$, and from (Equation A2) one obtains

$$\Delta m_{ox} = 5.524 \left(\frac{1 + 1.535\gamma}{1 + 3.957\gamma} \right) \Delta m_{obs} \qquad (A3)$$

The corrective term, $f(\gamma)$, accounting for the species incorporation is then given by

$$f(\gamma) = \frac{1 + 1.535\gamma}{1 + 3.957\gamma} \qquad (A4)$$

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