

Characterization of porous aluminum oxide films by metal electrodeposition

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Abstract—It is well known that porous (with underlying compact oxide) aluminum oxide films of varying pore size and diameter can be formed electrochemically on the surface of aluminum, depending on the oxidation conditions employed. In the present work, the properties of various porous Al oxide films were compared in terms of their electrochemical responses during silver electrodeposition. The cyclic voltammetric and current–time responses during silver deposition show an increased rate in the following sequence: sulfuric acid grown films (smallest pores), phosphoric acid grown (larger pores) and barrier oxide films (no pores), under identical applied voltages. Thicker porous oxide films formed after longer times of anodizing show lower deposition currents, while films formed at higher voltages (expected to yield larger diameter pores) result in higher silver deposition currents. Copyright © 1996 Elsevier Science Ltd

Key words: aluminum oxide, pore, porous, electrodeposition.

INTRODUCTION

The primary impetus of this work has been our general interest in establishing the structural properties, often at the nanometer scale, of oxide films formed electrochemically at Pt, Pd, Ir, Ni and Co, and, more specifically, in the detection and characterization of the size and structure of film pores. Although *ex situ* techniques such as scanning and transmission electron microscopy (SEM, TEM) can provide some information of this kind, these techniques involve the transfer of films to a high vacuum environment, which, together with the required sample preparation methods, may alter the film structure. For these reasons, *in situ* approaches, including scanning tunneling or atomic force microscopies (STM, AFM), would be desirable, even though the STM/AFM techniques may not be particularly useful for the investigation of highly porous, possibly rough (at the 1–10 nm scale) surfaces. Therefore, in the present work, we have attempted to use a simple *in situ* electrochemical approach for film characterization, *ie*, cyclic voltammetry (CV) and current–time measurements during metal (silver) deposition.

Electrochemically formed aluminum oxide films were initially selected for these studies as they have a well-known porous structure, with pores of controllable distribution and dimensions (Fig. 1)[1, 2]. The properties of these oxide films depend primarily on the anodizing conditions employed, *ie*, on the choice of solutions, anodizing voltage and time, *etc*. Silver was chosen in the present study as the metal to be electrodeposited on Al oxide films formed under a range of conditions. Metal electroplating, *eg*, of Ni and Ag[3] and Sn and Co[4] on anodically formed porous aluminum oxide films has long been used for the coloring of aluminum for decorative purposes as it produces an aesthetically pleasing finish, as well as for applications in magnetic memories and recording devices[5]. In most of these cases, the metal was deposited using *ac* conditions, while in the present study, *dc* conditions have routinely been employed.

Fundamental studies of the deposition of metals at Al oxide films have included the work of Gileadi and coworkers[6, 7], who studied copper and silver electrodeposition on porous aluminum oxide films in order to establish the mechanism of metal plating and to improve metal adhesion. Recently, porous aluminum oxide films have attracted considerable attention as a uniform nanostructural template at which metals and semiconductors of controllable

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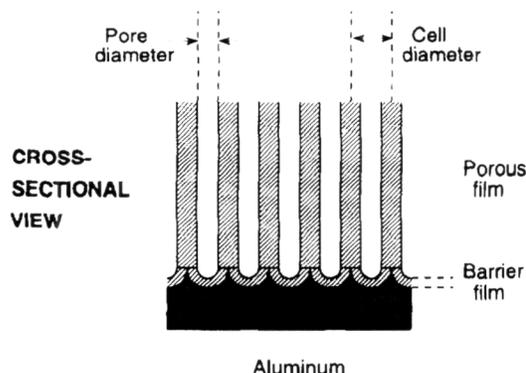


Fig. 1. Schematic diagram of porous oxide film structure formed electrochemically above barrier film on aluminum.

morphology can be deposited[8, 9]. These deposits have then been used as microelectrodes and as magnetic recording media. Moskovits *et al.* have investigated the optical and magnetic properties of metal particles (Fe, Ni, Ag, Au) electrodeposited in anodic Al oxide pores[10–13]. Martin *et al.* used aluminum oxide films as nanotemplates for the deposition of metals[14, 15] as well as polymers[14] and then studied the optical properties of these materials. Miller and Majda[16] reported the electrochemical behavior of aluminum oxide films impregnated with poly(4-vinylpyridine).

In the present work, the electrochemical signature observed using cyclic voltammetry and current–time measurements during the electrodeposition of silver at barrier Al oxide films at several different porous Al oxide surfaces has been compared. A clear correlation between the response and the expected morphology of the film has been observed.

EXPERIMENTAL

The working electrodes (*we*) were polycrystalline aluminum rods (*we*-1: 99.999% purity, Aldrich, 5.5 mm dia.; *we*-2: 99.9995% purity, Johnson Matthey, 6.4 mm dia.), embedded in insulating acrylamide resin (Scandiplast 9101, ScanDia, Germany). Only the exposed end (*we*-1 *ca* 0.24 cm², *we*-2 *ca* 0.32 cm²) of the electrode was electrochemically oxidized. The *we* surface was prepared by cutting the Al rod at 1000 rpm on a lathe, sonication in acetone for 5 min, followed by rinsing with triply distilled water. A large area Pt gauze was utilized as a counter electrode (*ce*). The saturated sodium calomel (*ssce*) electrode was used as the reference electrode (*re*) during the metal electrodeposition experiments. The *re* was placed in a separate cell compartment and was connected to the working electrode compartment through a closed wet ground-glass stopcock and a Luggin capillary.

Al oxide films were formed by anodic oxidation at constant cell potential using either a Kepco ATE

55-10M power supply or a HA-3-1 Hokuto Denko potentiostat, and the current–time response during anodization was recorded using a Linear Instruments model 585 strip chart recorder. The selected anodizing voltages ranged from 10 to 50 V, with anodizing times ranging from 5 min to 2.5 h. A Hokuto Denko HA-3-1 potentiostat and EG&G 175 programmer were utilized in all cyclic voltammetric (CV) experiments and the resulting voltammograms were plotted on a Hewlett Packard 7044A X-Y recorder.

Barrier oxide films were formed in neutral (pH 7) solutions of 0.5 M boric acid/0.025 M sodium tetraborate, while porous oxide films were prepared in 1.5 M sulfuric acid or 0.4 M phosphoric acid solutions. Silver electrodeposition was carried out from either acidic (0.1 M sulfuric acid) or neutral (0.5 M boric acid/0.025 M sodium tetraborate) solutions of 5 mM silver sulfate or 10 mM silver nitrate. All solutions were made up using triply distilled water and were deaerated with nitrogen before the metal deposition measurements. All experiments were carried out at room temperature.

RESULTS AND DISCUSSION

(a) Formation of anodic oxide films on aluminum

The typical current transients observed during the anodic oxidation of aluminum at two potentials (10 and 20 V) in acidic solutions (H₂SO₄) and also at 20 V in a neutral borate solution are represented in Fig. 2. In the neutral solution, steady-state currents of 2 μA or less are generally observed after *ca* 10 min at a constant potential of *eg*, 20 V. The exponential decay of the current with time, observed in these neutral solutions (pH 7), reflects the formation of a compact, barrier oxide film by the high-field ionic migration mechanism[17]. The thickness of the barrier layer is determined primarily by the anodizing voltage but also depends on the solution medium employed. The anodizing ratio, *i_e*, the barrier film thickness per applied voltage, has been reported to be in the range of 1.2 nm/V[18] to 1.7 nm/V[19] in borate solutions, although 1.4 nm/V is the most frequently quoted ratio for Al oxide films formed in borate solutions[3].

In acidic solutions, a sharp rise of the current (Fig. 2) upon the initial application of an anodic potential is followed by a rapid current decay during the first few seconds of anodization. This is associated with the initial onset of barrier oxide film formation. The current then increases again until it reaches a steady-state value for the leakage current[17] of *ca* 10 mA at 20 V and 1.5 mA at 10 V, reflecting the relatively high rate of dissolution of the barrier oxide film and its rapid conversion to form a porous oxide layer above the compact oxide film in the sulfuric acid medium. The underlying barrier film has been reported to have an anodizing ratio in the range

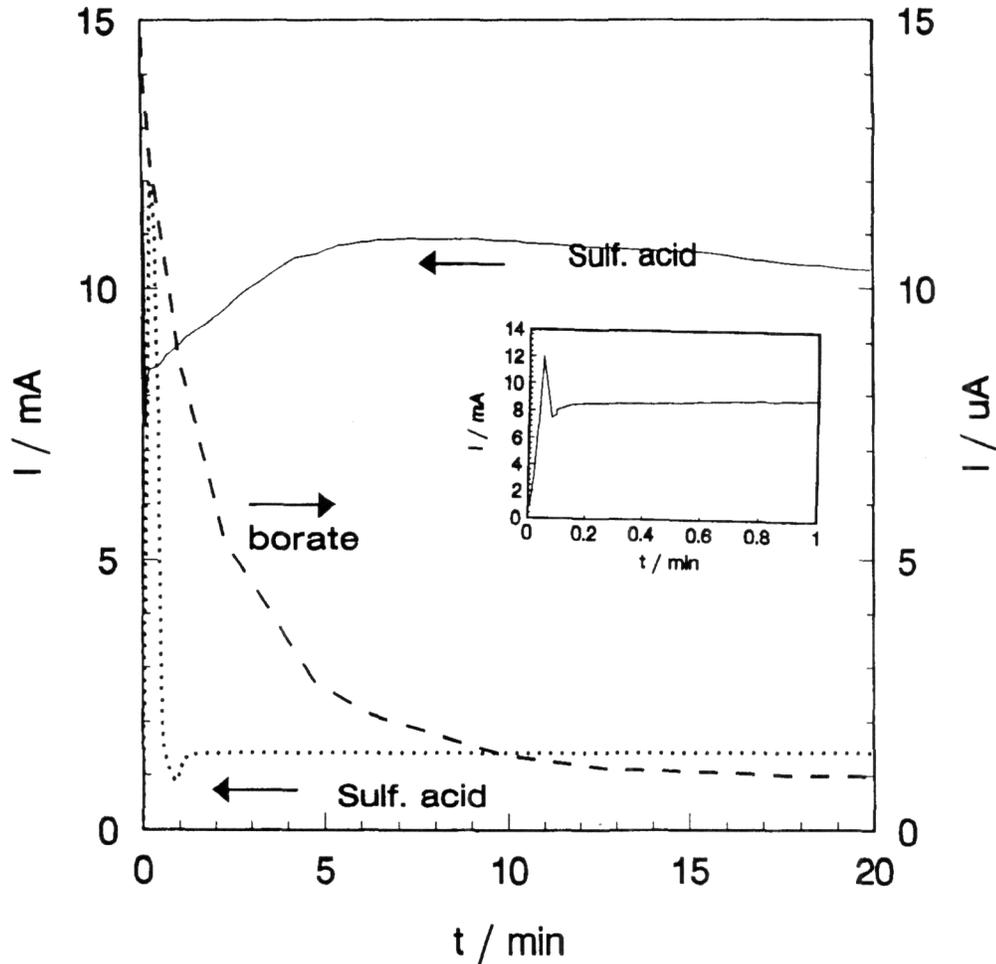


Fig. 2. Current measured during formation of barrier oxide film in borate (---) buffer solution at 20 V, and of porous oxide film in 1.5 M sulfuric acid solution upon application of 20 V (—) and of 10 V (⋯). The electrode area is *ca* 0.2 cm². The inset shows current during first minute of porous oxide formation in H_2SO_4 at 20 V.

of 1.0–1.3 nm/V [2, 17, 20, 21] for both sulfuric and phosphoric acid solutions.

Schnyder and Kötzt [22] have found that the thickness of porous films grown in 3 M sulfuric acid is directly proportional to the charge passed during anodizing, which can be quite significant. According to Patermarakis *et al.* [2], the limiting thickness of the porous oxide layer is reached when the somewhat conical pores which were originally separated by oxide walls begin to overlap towards the outer part of the film as a consequence of their increasing diameter. This limiting porous film thickness depends on the oxide growth conditions employed and can be as large as 120 μm , depending on the current density and temperature, while the pore diameter is determined mainly by the nature of the acidic solution employed.

Despite the fact that a wide range of growth conditions for porous oxide films is reported in the literature, there is general agreement that the pores of phosphoric acid grown oxide films are wider than those of oxide films formed in sulfuric acid[23].

For an applied potential of 20 V, some of the reported pore diameters for films grown in *ca* 1.5 M sulfuric acid are 12 nm[12], 15 nm[9], 20–22 nm (at current densities of 10–100 mA/cm²)[20] and 28 nm (at 5–75 mA/cm²)[2]. In phosphoric acid, which is typically used at a 4% (*ca* 0.4 M) concentration, the range of pore diameters appears to be 33 nm[6, 12], 28 nm (calculated using a growth rate of 1.29 nm/V)[24] and 32 nm (growth rate estimated to be 1.4 nm/V)[16]. Based on these literature data, and considering that in the present work, a constant applied potential was used to form oxide films, it is assumed that oxide films formed at 20 V for 20 min have pore diameters in the range of 12–15 nm when formed in sulfuric acid and 30–33 nm when grown in phosphoric acid.

(b) Electrochemical response during silver electro-deposition on aluminum oxide films: cyclic voltammetric response

The principal goal of these experiments was to establish whether Ag could be deposited with equal

ease on both barrier and porous Al oxide films and to determine whether any difference in the response during metal deposition could be discerned for films having relatively narrow pores (*eg* lower voltages) [20, 24] or longer pores (*eg* longer times of anodization)[22]. Also, it was of interest to compare Ag deposition at sulfuric (narrower pores) vs phosphoric (wider pores)[12] acid grown porous oxide films.

Figure 3 illustrates the typical cyclic voltammograms (CVs) obtained during silver deposition from a 5 mM silver sulfate solution in 0.1 M sulfuric acid at a variety of substrates. Figure 3(a) shows the typically unhindered process observed on a polycrystalline Pt electrode, while CVs (b)–(e) correspond to silver deposition on Al oxide substrates. The anodically formed films (CVs (c)–(e)) were all formed for 20 min at 20 V in their respective solutions. As can be seen from Fig. 3, the rate of silver deposition depends significantly on the properties of the substrate. Metal deposition is clearly the most rapid on Pt (Fig. 3(a)) and the deposited silver can be

readily reoxidized and removed during the anodic sweep; also, the current–voltage curve does not change with repeated cycling. At the air-formed oxide film (Fig. 3(b)), the CV is quite similar to that obtained at Pt, although the currents are somewhat lower and the overall CV appears somewhat more resistive. At barrier Al oxide films (Fig. 3(c)), the shape of the CV for the silver deposition is now different, reflecting the presence of a thicker oxide film with limited electronic conductivity. Silver deposition at the porous oxide films is substantially more inhibited, as seen by the reduced currents in Fig. 3(d) and (e). The lowest currents are seen for sulfuric acid formed films, which are known to have the smallest pores, as discussed earlier [9, 12, 24], but should otherwise have an underlying barrier film of similar thickness to the oxides studied in Fig. 3(c) and (d) [2, 20, 21].

Figure 4 show several particular examples of CVs obtained with time of cycling during silver deposition for phosphoric acid grown films, formed in 10 min 55 V (Fig. 4(a)) and 20 min at 20 V (Fig. 4(b)). It can be seen that silver deposition is hindered more by longer times of anodization (longer pores, thicker porous oxide film) than by higher voltages (thicker barrier oxide film). This is an important result, as it suggests that metal deposition is a very good indicator of the properties of the porous vs. barrier oxide film. Notably, at identical conditions of voltage and time, the rate of metal deposition is much smaller in CV experiments carried out at sulfuric acid grown porous oxide films, which are expected to have a very similar barrier oxide film thickness[2, 17, 20, 21], but substantially different pore structures.

Some hysteresis in the cathodic current is seen in Fig. 3(c)–(e) and Fig. 4, in particular, especially in the first few cycles of potential, in which the silver deposition rate in the cathodic scan (at potentials negative of the reversible potential for Ag deposition) is lower than in the subsequent anodic sweep. This hysteresis is likely to be a reflection of the mechanism of Ag deposition, in which the rate of deposition is controlled by the nucleation and growth of silver[25]. In the case of Pt, a reversal of potential in the CV at the early stages of Ag deposition, *eg*, at *ca* 0.4 V, when the currents would be as low as in the case of the Al oxide substrates, would be expected to result in a similar type of hysteresis response. In Fig. 3(a), silver deposition at Pt is so facile that it is already diffusion controlled at *ca* 0.38 V, with the rate limited by the diffusion of silver ions in solution to the Pt surface.

Silver deposition rate control by nucleation and growth at these anodically formed Al oxide substrates is also consistent with the fact that the silver deposition currents in CV experiments increase in magnitude with continuous potential cycling (Fig. 4), *ie* as a greater number and larger silver nuclei develop with cycling time (Ag is not oxidized in the anodic sweeps), the higher is the rate of further Ag deposition. Interestingly, after some charge density

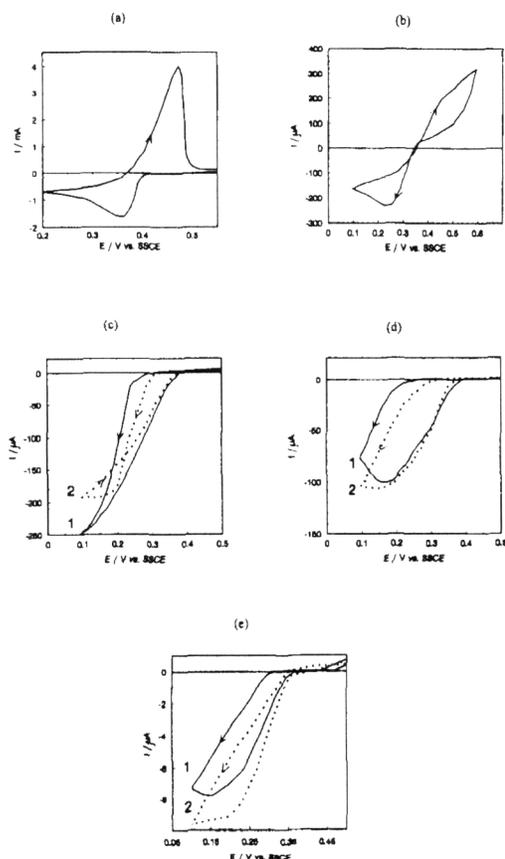


Fig. 3. CV response during silver deposition from 5 mM Ag_2SO_4 in 0.1 M H_2SO_4 on (a) Pt; (b) thin air-formed aluminum oxide film; (c) aluminum oxide grown in pH 7 solution, (1) first cycle, (2) second cycle; (d) 0.4 M H_3PO_4 , (1) first cycle, (2) second cycle; and (e) 1.5 M H_2SO_4 , (1) first cycle, (2) second cycle. Sweep rate 10 mV s^{-1} for phosphoric acid, all others 20 mV s^{-1} . The electrode area is *ca* 1.5 cm^2 for Pt and *ca* 0.2 cm^2 for Al.

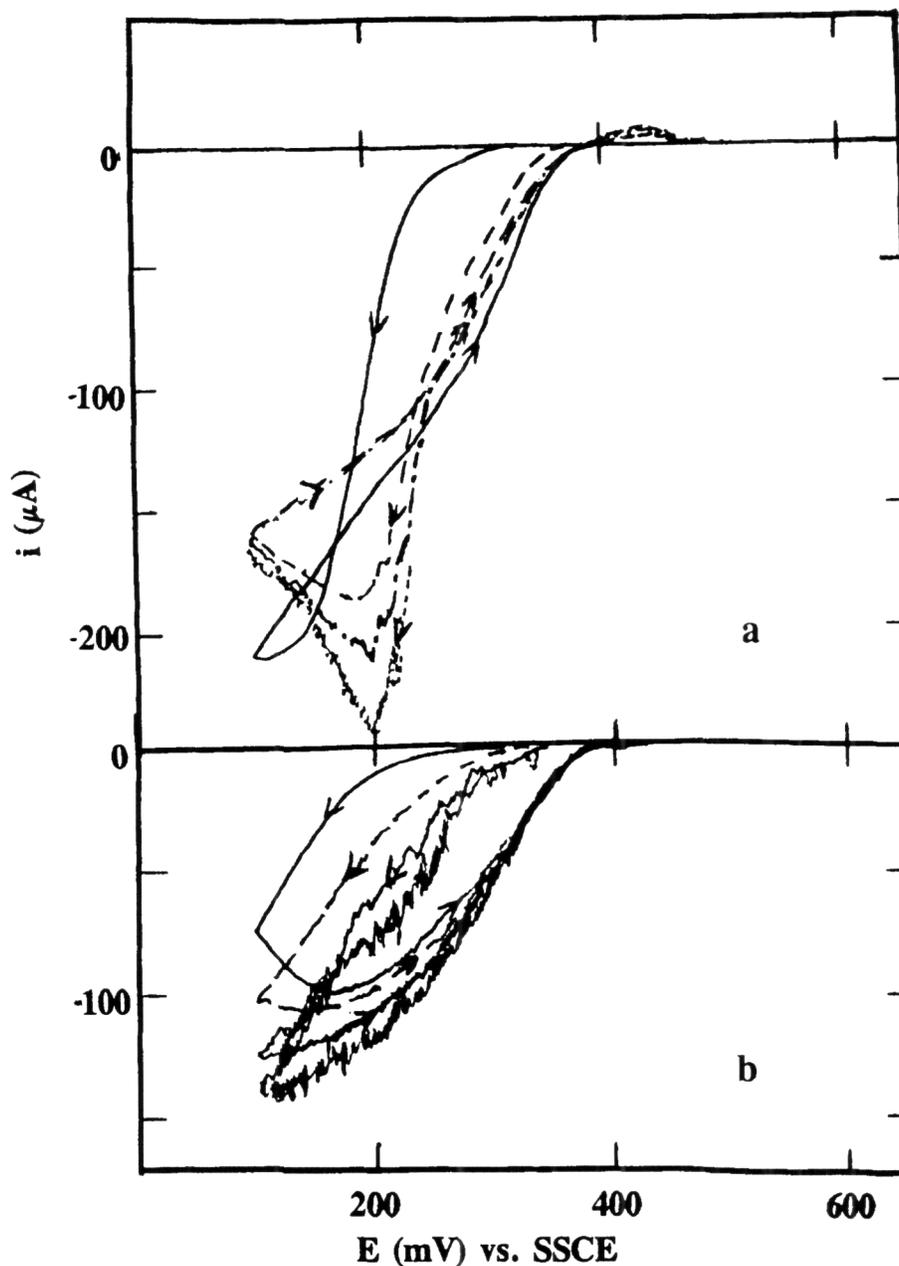


Fig. 4. Cyclic voltammograms during silver deposition from 5 mM Ag_2SO_4 in 0.1 M H_2SO_4 on aluminum oxide grown in 0.4 M H_3PO_4 for 10 min at 55 V (a) and for 20 min at 20 V (b). Sweep rate 10 mV s^{-1} . Solid line shows first cycle, currents increase with further cycling.

has passed, the CV currents become rather noisy. If it is assumed in the case of porous films that silver is initially depositing in the oxide film pores, then the onset of noise may reflect the fact that silver deposition in the pores is now complete and subsequent silver deposition is occurring on the outer surface of the oxide film, as can be seen visually. The possible development of a high surface area, fragile dendritic silver deposit at this stage could make the rate of further silver deposition dependent on mass transport in solution, *ie* either by diffusion or convection, hence leading to the noisy current response.

The absence of almost any silver oxidation current in Figs 3(c)–(e) and Fig. 4 reflects the valve-like character of Al oxide films, such that electrons can pass readily from the metal to the solution, *ie* cathodically, but not in the reverse direction.

(c) Electrochemical response during silver electrodeposition on aluminum oxide films: current–time transients

The results of potential step experiments ($E_{\text{init}} = 0.5 \text{ V}$, $E_{\text{final}} = 0.1 \text{ V}$ vs *sce*) in which the current passed during silver electrodeposition was

monitored as a function of time at a range of Al oxide substrates are shown in Fig. 5. At barrier oxide films formed in borate solutions, the higher the anodizing voltage, *ie*, the thicker the barrier oxide film[3], the lower the magnitude and the longer the time of the current peak. After the current peak, the current appears to fall off in a manner independent of the anodizing time and voltage. Figure 5 also confirms the results of Figs 3 and 4, in that the silver deposition currents are substantially lower at porous Al oxide films, even when formed at the same voltage as the barrier oxide films. Also, sulfuric acid grown films, expected to have the narrowest pores[9, 12, 20], give the smallest silver-deposition currents, while in phosphoric acid, it is seen that longer times of porous oxide growth (40 vs. 20 min), yielding longer oxide pores, result in a greater inhibition of silver deposition.

Figure 6 summarizes the results of Fig. 4, showing the charge passed during silver deposition at phosphoric acid grown films of various expected thicknesses and pore diameters. At constant voltage (constant barrier film thickness), longer anodization times cause a drop in the rate of silver deposition, due to the lengthening of the oxide film pores with time. At constant anodization times, the rate of deposition of silver increases with anodizing voltage, consistent with the expected increase in pore diameter and hence enhanced available surface area for metal deposition. It should be noted that if the increased barrier film thickness formed at higher voltages were playing a significant role here, then less metal deposition could be expected for higher voltages. These results show that oxide film morphology is being tracked by the CV and *i/t* response during silver deposition, yielding

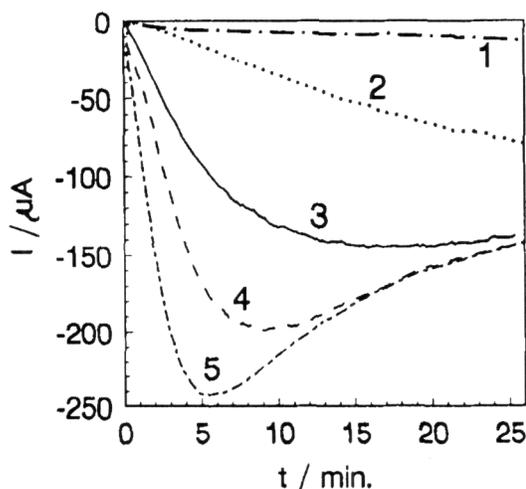


Fig. 5. Chronoamperograms ($E_{\text{init}} = 0.5 \text{ V}$, $E_{\text{final}} = 0.1 \text{ V}$ vs. *sce*) of silver deposition from 5 mM Ag_2SO_4 in 0.1 M H_2SO_4 on aluminum oxide films formed in: sulfuric acid solution at 20 V for 20 min (1); phosphoric acid at 20 V for 40 min (2) and 20 V for 20 min (3); and borate solutions at 20 V for 20 min (4) and 10 V for 10 min (5).

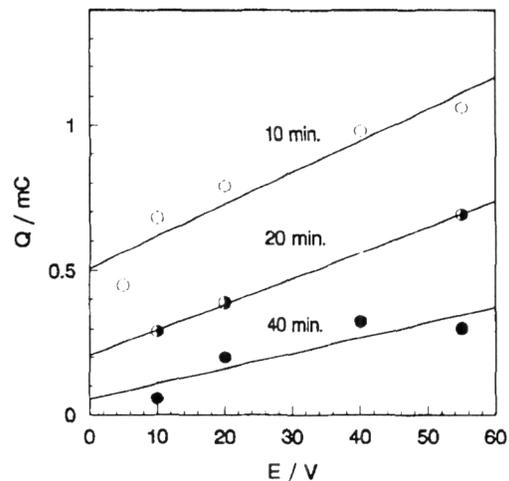


Fig. 6. Silver deposition charge passed in the first cathodic scan on phosphoric acid grown aluminum oxide, as a function of anodization voltage and time: 10 min (○), 20 min (◐) and 40 min (●).

the most facile metal electrodeposition for thin porous oxide films, formed at the shortest times, and for films of the largest pore diameters (formed at high voltages).

In the experiments shown in Figs 3–6, Ag was electrodeposited in all cases from a Ag-containing sulfuric acid solution. Since it was considered possible that the acidic solution could slowly dissolve the Ag-coated Al oxide films and hence undermine the validity of the interpretation of the data, another set of silver deposition experiments was carried out using neutral 10 mM silver nitrate in a pH 7 borate buffer medium. Both the CV and *i/t* signatures observed during Ag deposition at the various substrates under study were very similar to those obtained in the sulfuric acid medium and the trends seen in Figs 3–6 were reproduced exactly. However, silver deposition from the borate solution did result in lower metal deposition rates (currents) overall, possibly due to a higher solution *iR* drop caused by the lower conductivity of the solution. Also, the potential for Ag deposition shifted negatively from *ca* 0.4 V in the acidic plating solution to 0.25–0.3 V vs *sce* in the borate medium. This may indicate some complexation of Ag^+ by the tetraborate anion, which could also lower the rate of silver deposition, as the activity of free silver ion would be reduced.

SUMMARY

The above results show that increasing the thickness of the barrier oxide film formed on Al does reduce the rate of Ag deposition, as expected. Significantly, however, the silver deposition rates are greatly affected by the thickness and pore sizes of porous Al oxide films. The rate is substantially slower

when pore diameters are small, *ie*, for sulfuric vs. phosphoric acid films, and also when lower voltages are employed. Also, silver deposition is significantly inhibited as porous oxide films are made thicker (longer times of anodization) and hence as pores are made longer.

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