Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Thin Solid Films 471 (2005) 118–122

thin solid films

www.elsevier.com/locate/tsf

Composition and density of non-thickness-limited anodic films on aluminium and tantalum

Q. Lu[a], P. Skeldon[a,*], G.E. Thompson[a], H. Habazaki[b], K. Shimizu[c]

[a] *Corrosion and Protection Centre, University of Manchester Institute of Science and Technology, P.O. Box 88, Manchester M60 1QD, UK*
[b] *Graduate Engineering School, Hokkaido University, N13 W8, Kita-ku, Sapporo 060-8628, Japan*
[c] *University Chemical Laboratory, Keio University, 4-1-1 Hiyoshi, Yokohama 223, Japan*

Received 22 October 2003; received in revised form 23 April 2004; accepted 28 April 2004
Available online 22 September 2004

Abstract

The unusual occurrence of anodic films of unlimited thickness has been recently reported for anodizing of tantalum in certain dehydrated, high-temperature electrolytes with organic solvents. The precise nature of these films is still uncertain. In the present work, non-thickness-limited (NTL) anodic films were formed at 0.1 mA cm^{-2} on aluminium and tantalum in glycerol/phosphate electrolyte at 453 K and then examined by Rutherford backscattering spectroscopy (RBS). The results disclosed films composed of alumina and tantala, free of phosphorus species at the resolution of the measurements. Most notably, the densities of the NTL alumina and tantala were about 2.4 and 3.6 g cm^{-3}, respectively. These values are less than those of compact anodic films of the type usually grown at high efficiency in aqueous electrolytes by respective factors of about 1.3 and 2.2. This difference in density is attributed primarily to the morphology and structure of NTL film materials, which incorporate significant porosity.

Keywords: Tantalum; Aluminium; Anodizing; Anodic films; NTL

1. Introduction

Non-thickness-limited (NTL) anodic films are formed on tantalum in dehydrated electrolytes comprising either glycerol or mannitol as solvent, with a wide range of solutes, at temperatures above 423 and 513 K, respectively [1]. These recently discovered films thicken under an apparently low electric field, no more than 10^5 V cm^{-1}, without restriction on the thickness [2]. For instance, under potentiostatic conditions of growth, the characteristic decay of current density, typical of usual high-field anodic tantala grown in aqueous electrolytes, is temporary, since the current then recovers to sustain significant film thickening over the macroscopic substrate surface [1]. Correspondingly, under galvanostatic conditions, the familiar linear voltage rise associated with conventional anodizing is brief, with the voltage then declining, such that the thickness restriction of dielectric breakdown is not met [2,3]. The limited analyses of the NTL films, by energy dispersive X-ray (EDX) analysis and X-ray photoelectron spectroscopy (XPS) [1,3], indicate a composition close to that of tantala. The dielectic constants of the films exceed those of usual anodic tantala, with values of 147 [1] and 50 [3] reported compared with about 27 for the conventional anodic film material. In cross-sections examined by transmission electron microscopy (TEM), two film regions are distinguishable, both of amorphous or microcrystalline appearance [2,4]. The thickness of the inner region, adjacent to the metal, is close to the product of the projected formation ratio for high-field tantala at the relevant temperature, derived using the kinetic relationship for film growth established at lower temperatures, and the final anodizing voltage. Thus, this thickness dependence suggests that the inner region is similar to conventional anodic tantala, which is also consistent with its uniform, featureless appearance in the TEM images. The outer region has a subtle texture, with suggestions of linear features, which contrasts with the inner region. Cross-sections of the outer region taken parallel to the metal surface disclose numerous light spots, with diameters of a few nanometres and with separations of about 30 nm. These spots have been interpreted as pores that extend from the film

---

[*] Corresponding author. Tel.: +44-161-200-4872; fax: +44-161-200-4865.
E-mail address: p.skeldon@umist.ac.uk (P. Skeldon).

doi:10.1016/j.tsf.2004.04.061

surface to the inner film region. Thus, a model of growth has been proposed [4] in which a normal barrier film transforms to porous-type film, with similarity to the well-known formation of porous anodic alumina [5]. However, it has also been proposed that the NTL film is a uniform material that contains a high concentration of oxygen vacancies [1]. The vacancies result from the absence of hydroxyl species in the dehydrated electrolyte and facilitate ionic transport at low fields [1]. Irrespective of the model, NTL growth is terminated rapidly by addition of water to the electrolyte [1,3]. Although less studied than tantalum, NTL films can also be formed on aluminium [1,4], with TEM evidence revealing similarity with porous anodic alumina of lower temperature, aqueous electrolytes [4].

In order to understand further the nature of NTL films, Rutherford backscattering spectroscopy (RBS) has been employed to determine the compositions and densities of NTL films formed on tantalum and aluminium. The anodizing behaviours and the morphologies of the films have been reported previously [2,4].

2. Experimental details

Tantalum layers, of thickness about 350 nm, were deposited by magnetron sputtering, using an Atom Tech system, onto anodized aluminium substrates. The source material was 99.9% tantalum. The pressure in the chamber prior to deposition was 3×10^{-5} Pa. Sputtering was carried out using 99.998% argon at 0.5 Pa. After masking to define a working area of about 1 cm^2, specimens were anodized at 0.1 mA cm^{-2} in 10 wt.% dibasic potassium phosphate in glycerol at 453 K, using a two-electrode cell with a platinum cathode. The electrolyte was dried previously at 453 K for 2 h [1]. Anodizing was also carried out for 99.99% aluminium sheet that had been first electropolished for 300 s in perchloric acid/ethanol at 278 K. Anodizing times for the various specimens are given in Table 1. The voltage–time responses, revealing an initial voltage increase with time followed by a reducing voltage for tantalum or approach to a constant value for aluminium, have been reported previously [2,4]. Control specimens with compact anodic alumina and anodic tantala films were prepared by anodizing electropolished aluminium to 200 V at 5 mA cm^{-2} in 0.1 M ammonium pentaborate solution at 293 K, and by anodizing sputtering-deposited tantalum to 150 V at 0.1 mA cm^{-2} in 0.06 wt.% phosphoric acid solution at 358 K. Such conditions allow formation of anodic films at high efficiency, with negligible loss of species to the electrolyte. Surfaces of specimens were examined by RBS using 2.0 MeV He^+ ions with a current of 60 nA and beam diameter of 1 mm. The beam was incident normal to the surface of the specimen, with scattered ions detected at 165° to the direction of the incident beam. The data were interpreted using the RUMP program [6]. The atomic density of film material was assumed to be 9.15×10^{22} and 7.67×10^{22} atoms cm^{-3} for films on aluminium and tantalum, respectively. The densities correspond to mass densities of about 3.1 and 8.0 g cm^{-3}, which are the values appropriate to compact anodic alumina and anodic tantala [7,8].

3. Results

3.1. NTL films on aluminium

Two NTL films on aluminium were examined by RBS, with spectra compared with that of a conventional, compact, barrier-type anodic film formed to 200 V in ammonium pentaborate electrolyte. The thicknesses of the NTL films were determined previously by TEM (Table 1) [4], with films comprising 95% and 98% of porous zouter region material, while that of the control film is known from the established formation ratio of 1.2 nm V^{-1} for the selected conditions of anodizing [9]. Superposition of the RBS spectra indicated the formation of anodic alumina films differing significantly only in respect of their thickness (Fig. 1(a)). The simulations of the data (see example of Fig. 1(b)) indicated thicknesses of 185 and 345 nm for the NTL films, with the thickness increasing with the time of anodizing, and the expected value of 240 nm for the control film. The accuracy of the measurements cannot exclude the possibility of a few percent difference in the O/Al atomic ratios between specimens. No signal from phosphorus was resolved for the NTL films, with an upper limit on the P/Al atomic ratio of 0.01. One specimen revealed some chloride contamination at the surface, giving rise to a small peak, superimposed on the pile-up background, just ahead of the calculated position of phosphorus at the surface (Fig. 1(a)). From the cation charges in the films and the

Table 1
Summary of results from TEM and RBS for anodic films formed on aluminium and tantalum

Specimen	Anodizing time (ks)	TEM inner region (nm)	TEM film thickness (a) (nm)	RBS film thickness (b) (nm)	Ratio (a)/(b)	Charge (c) film cations ($\mathrm{C\ cm}^{-2}$)	Charge (d) in cell ($\mathrm{C\ cm}^{-2}$)	Ratio (c)/(d)	Outer region TEM/RBS
Al (NTL)	7.2	12 ± 3	243 ± 7	185 ± 9	1.31 ± 0.07	0.33 ± 0.02	0.72 ± 0.04	0.46 ± 0.03	1.34 ± 0.09
Al (NTL)	12.6	12 ± 3	545 ± 30	345 ± 17	1.58 ± 0.12	0.61 ± 0.03	1.26 ± 0.06	0.48 ± 0.03	1.60 ± 0.12
Al (control)	0.087	–	240 ± 8	240 ± 12	1.00 ± 0.06	0.42 ± 0.02	0.44 ± 0.02	0.95 ± 0.07	–
Ta (NTL)	38.6	9 ± 3	609 ± 10	295 ± 15	2.06 ± 0.11	0.52 ± 0.03	3.86 ± 0.19	0.13 ± 0.01	2.10 ± 0.13
Ta (NTL)	19.0	100 ± 5	700 ± 20	359 ± 18	1.95 ± 0.11	0.63 ± 0.03	1.90 ± 0.10	0.33 ± 0.02	2.32 ± 0.19
Ta (control)	5.6	–	288 ± 8	290 ± 15	0.99 ± 0.06	0.51 ± 0.03	0.56 ± 0.03	0.91 ± 0.06	–