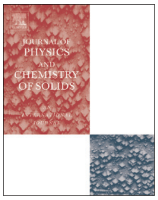
Journal of Physics and Chemistry of Solids 85 (2015) 278–286

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs



Investigation of the growth and local stoichiometric point group symmetry of titania nanotubes during potentiostatic anodization of titanium in phosphate electrolytes

F.R. Cummings [a,*], T.F.G. Muller [b], G.F. Malgas [b], C.J. Arendse [b]

[a] *Electron Microscope Unit, University of the Western Cape, Robert Sobukwe Drive, Bellville 7535, South Africa*
[b] *Physics Department, University of the Western Cape, Robert Sobukwe Drive, Bellville 7535, South Africa*

ARTICLE INFO

Article history:
Received 8 February 2015
Received in revised form
3 June 2015
Accepted 10 June 2015
Available online 12 June 2015

Keywords:
Nanostructures
Oxides
Crystal growth
Electron energy loss spectroscopy
Crystal structure

ABSTRACT

Potentiostatic anodization of commercially pure, 50 μm-thick titanium (Ti) foil was performed in aqueous, phosphate electrolytes at increasing experimental timeframes at a fixed applied potential for the synthesis of titania nanotube arrays (TNAs). High resolution scanning electron microscopy images, combined with energy dispersive spectroscopy and x-ray diffraction spectra reveal that anodization of the Ti foil in a 1 M NaF+0.5 M H_3PO_4 electrolyte for 4 h yields a titanate surface with pore diameters ranging between 100 and 500 nm. The presence of rods on the Ti foil surface with lengths exceeding 20 μm and containing high concentrations of phosphor on the exterior was also detected at these conditions, along with micro-sized coral reef-like titanate balls. We propose that the formation of these structures play a major role during the anodization process and impedes nanotube growth during the anodization process. High spatially resolved scanning transmission electron microscopy-electron energy loss spectroscopy (STEM-EELS) performed along the length of a single anodized TiO_2 nanotube reveals a gradual evolution of the nanotube crystallinity, from a rutile-rich bottom to a predominantly anatase TiO_2 structure along its length.

1. Introduction

With the advent of nanoscience researchers and technologists have employed low cost, self-assembled nanotubes with enhanced surface-to-volume ratios and size-dependent properties in various devices, with the aim of improving the efficiency and lowering the manufacturing cost of the underlying device. One group of nanotubes that is particularly interesting and already found a wide range of applications, including photovoltaics [1,2], photo-catalysis during the hydrolysis of water [3,4], hydrogen production [5], renewable, high storage batteries [6] and oxygen sensors [7], is TiO_2 nanotubes (TNTs) and TNAs [8].

The formation of these structures is based on a well-known process whereby compact oxide layers are grown on top of transition metal substrates during potentiostatic or galvanostatic anodization in aqueous, low pH electrolytes [9,10]. Innovative approaches and modifications to the traditional anodization technique have led to transformation of the thick oxide layer into nanotubes in the presence of fluoride rich electrolytes [8]. Large volumes of literature [e.g. 11–13] have been published in the last decade on improving the synthesis of TNAs, with various novel structures with high aspect ratio achieved. For example, recent work by Song et al. [14] have shown that by altering the traditional direct current during anodization, a significantly faster growth rate of the nanowire arrays is attainable. The resulting nanotube morphology showed ultrahigh aspect ratios with improved photon-to-electron conversion properties. Elsewhere Chen et al. [15] demonstrated high accuracy in the control of the nanotube pore distribution, by synthesizing regionally distributed TiO_2 nanotube arrays using a one-step anodization process of Ti foil in combination with an adjacent Ti strip; the resulting nanotube architecture showed that the nanotube density could be controlled over a wide range in the Ti foil specific region, while keeping no tube in the adjacent Ti strip region. These examples demonstrate the potential importance of these novel nanostructures in advanced technological applications.

However, a complete understanding of the self-assembled growth process of TNAs during the anodization process remains in its infancy stage for various reasons. For example, to date no feasible literature has been published on the rate-limiting factors contributing to the film growth. High applied voltages and high

---

[*] Corresponding author. Fax: +27 21 959 9378.
E-mail address: fcummings@uwc.ac.za (F.R. Cummings).

http://dx.doi.org/10.1016/j.jpcs.2015.06.009
0022-3697/

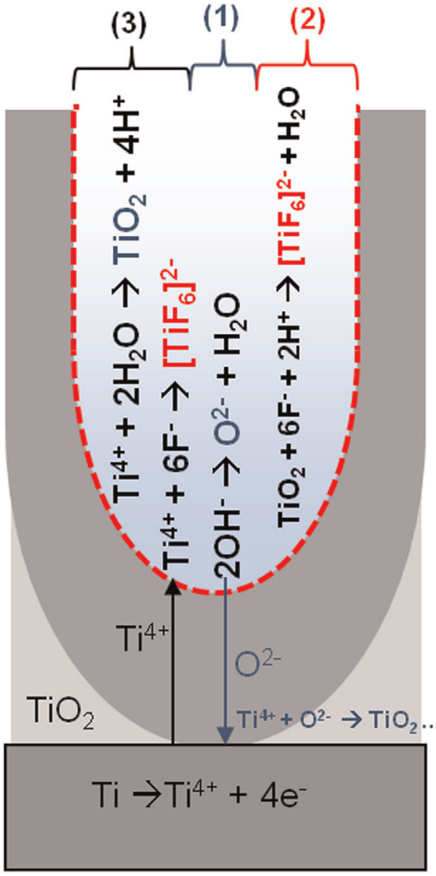


Fig. 1. Schematic representation of the TiO_2 nanotube growth process during anodization.

concentrations of ionic species in the electrolyte are often used in combination, with the results of two similar experiments varying appreciably. From a technological point-of-view, this lack of quantification of the growth process results in non-repeatable synthesis, which largely explains the relatively slow commercialization and large-scale application of these structures in advanced devices.

It goes without saying then that if TNTs and TNAs are to make a significant impact in the performance of their underlying application, understanding their growth mechanism during anodization is paramount as this will allow for accurate, controlled dimensions, which in turn will allow for tunable properties. The growth mechanism describing the formation of anodized TiO_2 nanotubes is presented in various publications [8,16–18]. According to the generally accepted model the main difference between the formation of oxide layers and nanotubes is the competition between anodic oxide formation (reactions 1 and 2 below) and chemical dissolution of the oxide as soluble fluoride complexes (reactions 3 and 4) as depicted schematically in Fig. 1.

$$Ti \rightarrow Ti^{4+} + 4e^- \quad (1)$$

$$Ti^{4+} + 2H_2O \rightarrow TiO_2 + 4H^+ \quad (2)$$

$$Ti^{4+} + 6F^- \rightarrow [TiF_6]^{2-} \quad (3)$$

$$TiO_2 + 6F^- + 4H^+ \rightarrow [TiF_6]^{2-} + 2H_2O \quad (4)$$

This model ostensibly well explains the growth of TiO_2 nanotubes as compared to oxide layer formation under ideal field-assisted conditions. However, a holistic description of all the processes occurring in the electrochemical bath, especially at the anodic interface, is rather lacking even though some of these adverse reactions play a crucial role in either assisting or preventing the formation of the nanotube structure. For example, it is well known [19,20] that some titanium oxides present a duplex layer that is susceptible to the incorporation of foreign ions from the electrolyte, which markedly affects the resultant material's structure and properties [21,22].

Phosphate electrolytes are particularly interesting since it is well reported that oxides grown on Ti substrates in these solutions contain a significant amount of phosphorous species [19]. The aim of this work is to explore the formation of nanotubes in these phosphorous rich electrolytes at standard anodization conditions. Previous studies [20,22] have shown that at low concentrations of PO_4^{3-}, nanotubes with a high concentration of phosphorous species on their exterior are attainable. In this work, the high concentration of PO_4^{3-} will allow for a concrete investigation into whether F^- incorporation by the thick TiO_2 layer is in direct competition with PO_4^{3-} absorption during the anodization process. If this is indeed the case, then it is expected that no nanotube formation is possible under such conditions, as the chemical dissolution of the oxide layer (Eqs. 3 and 4) is inhibited by the formation of some phosphate complex at the oxide surface.

A further point of interest from the generally accepted growth model of TiO_2 nanotubes is the lingering question regarding the actual stoichiometry of the resultant nanotube. For the most commonly used electrolytes the end result is usually arrays of nanotubes that are amorphous with a titanate stoichiometry, requiring post-anodization annealing in an oxygen rich ambient at elevated temperatures [23–25]. This implies that the as-anodized structures have local nearest neighbor point group symmetry around the Ti atoms that is sporadic and not regular. Upon annealing, generally between 400 and 500 °C, it is reported that the nanotubes form a hexagonally shaped bottom that has a rutile crystal structure, which evolves into anatase crystal along the length of the tube [14]; usually investigated using x-ray diffraction (XRD) studies. In this work this interesting characteristic of TNAs will be investigated by means of EELS at a spatial resolution of 0.2 nm using a scanning transmitted electron probe. This allows for probing the subtle changes in the crystal structure of the TiO_2 as a function of the nanotube length, ultimately giving a holistic view of the evolution of the crystalline structure.

2. Experimental

2.1. Anodization set-up

A standard anodization set-up was used in this study. The system employs a two electrode configuration during which a 1×1 cm^2 flag-shaped Pt grid electrode serves as cathode. Commercially pure Ti foil (Goodfellow, United Kingdom; 50 μm thick; 99.99% purity; 0.49 cm^2 area), placed against a stainless steel disc (1 cm in diameter) is contained within a polytetrafluoroethylene (PTFE) holder and acts as the anode during anodization. The PTFE holder exposes a Ti surface area of approximately 0.2 cm^2 to the electrolyte during operation. The two electrodes are placed in an electrolytic solution, submerged within an ultrasonic bath. The distance between electrodes is kept at 1 cm and a direct current (DC) variable power supply (maximum power output of 1 kW) is used to apply a potential difference between the electrodes. An ammeter is connected to the anode to monitor the changes in the current density at the Ti/electrolyte interface. Prior to anodization, the Ti foils were ultrasonically cleaned in acetone and methanol for 5 min each, washed in de-ionized water and left to dry in air. Once dry, the Ti substrate is placed in the PTFE holder and placed