Controlled spacing of self-organized anodic TiO$_2$ nanotubes

Selda Ozkan [a], Nhat Truong Nguyen [a], Anca Mazare [a], Isotta Cerri [b], Patrik Schmuki [a,c,*]

[a] Department of Materials Science, Institute for Surface Science and Corrosion WW4-LKO, Friedrich-Alexander University, Martensstraße 7, D-91058 Erlangen, Germany
[b] Toyota Motor Europe, Hoge Wei 33, 1930 Zaventem, Belgium
[c] Chemistry Department, Faculty of Sciences, King Abdulaziz University, 80203 Jeddah, Saudi Arabia

A B S T R A C T

We report on how to grow and control self-organized TiO$_2$ nanotube arrays that show defined and regular gaps between individual nanotubes. For this we use electrochemical anodization of titanium in fluoride containing diethylene glycol (DEG) electrolytes, with variations in voltage and water content in the electrolyte. In these specific electrolytes, such nanotubes show a true spacing, i.e. nanotubes are spaced both at top and at bottom in regular intervals, this in contrast to classic nanotubes obtained in other organic electrolytes showing a close-packed organization. We identify critical parameters that define the "region of existence" i.e. under which condition tube spacing occurs as well as the intertube distance, to be the voltage and the water content. Using these findings allows to grow tubes where diameter and spacing can even be independently controlled.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Since the first reports on nanotubes or nanopores growth on Ti or Ti alloys by electrochemical anodization by Assefpour-Dezfuly [1] and later by Zwilling et al. [2], Gong et al. [3] and Beranek et al. [4], TiO$_2$ nanotubes have been explored for a wide range of applications and have, over the past decade, become one of the most investigated 1D nanostructures. Remarkable progress has been made in improving the morphology of TiO$_2$ nanotubes (NTs) and nowadays a high control over morphology (diameter, length, open top surfaces, smoothness of tube wall, etc.) has been achieved [5,6]. In turn, the control over morphology enabled considerable progress in the application of these well-ordered nanostructures, in a variety of domains such as electrical and photoelectrical applications, photoelectrochemical water splitting and biomedical coatings or drug release systems [6]. Current efforts for further progress for example target an even further increased ordering of the tubes [7] or creating fully defined single-walled tubes [8,9].

Generally, NTs layers obtained in aqueous or organic electrolytes grow in a hexagonally close-packed configuration. This is not always apparent from top views as under many conditions nanotubes tend to grow in a bulb shape [6,10,11], but it is typically evident at the bottom growth front, close to substrate. Nevertheless, previous findings report that with certain electrolyte compositions, NTs growth with some spacing between individual tubes can be established. This particularly if the electrolyte is based, except for HF and H$_2$O, on DEG or di-methyl sulfoxide (DMSO) [12–15]. Over the years, few more electrolytes were reported to result in the growth of spaced or "loose-packed" NTs under specific anodization conditions e.g. ethylene glycol (EG), tri(tetra, poly)-ethylene glycol etc. [16–18].

Nevertheless, a systematic investigation of the key parameters that could be exploited to gain control over morphological features of such arrays, namely the intertube spacing, is missing.

In the present work, we evaluate and report the key anodization parameters that influence the occurrence (or not) of spaced tubes (as opposed to hexagonal close-packed tubes or other anodic oxide morphologies), and show how to control the morphology and spacing of these peculiar nanotube arrays.

2. Experimental

Ti foils (0.10 mm, 99.6%, Advent, England) were degreased by ultrasonication (acetone, ethanol and distilled water) and dried in nitrogen stream. Samples were pretreated (anodized and removal of nanotubes by ultrasonication), then anodized (in DEG + 4 wt% HF (40%) + 0.3 wt% NH$_4$F + 1 wt% H$_2$O), immersed in ethanol (1 h) and dried. An electrochemical set-up (IMP-Series Jaissle Potentiostat) with a two-electrode configuration (Pt counter electrode, Ti working electrode) was used. Different voltages (5–50 V) and different water contents were evaluated.

Samples' morphology was investigated using a scanning electron microscope (SEM) Hitachi FE-SEM 4800. All geometrical properties (outer diameter, spacing and wall thickness) were measured from SEM images (Image J software), and are the average of 15 measurements.

3. Results and discussion

Fig. 1 presents an example of spaced TiO_2 nanotubes obtained by anodization in the above described DEG (di-ethylene glycol) electrolyte, at 30 V for 4 h. In this case, individual tubes with 1.2 μm length and outer diameter of ≈150 nm grow, but compared to the generally reported close-packed configuration of NTs grown in classic electrolytes (e.g. aqueous or organic), an organized spacing in between the nanotubes is clearly apparent. At the top, the average spacing is 109 ± 46.7 nm. Most important, to verify a true spacing in between the tubes, nanotube layers were cracked-off close to their substrate i.e. directly at their base, see Fig. 1c. From the SEM images, it is evident that also at the bottom, spacing is established; an average tube to tube distance of 106 ± 25 nm is obtained. In other words, bottom and top spacing are in a very similar range, reflecting an almost cylindrical outer tube shape.

A schematic representation of such spaced nanotubes is shown in Fig. 1d defining the main morphological parameters that will be further evaluated (outer diameter, spacing, wall thickness).

In the present case, i.e. for an electrolyte composition of 4 wt% HF, 1 wt% H_2O and 0.3 wt% NH_4F in DEG, a controlled variation over the intertube spacing can be achieved through the applied voltage; at 10 V a spacing of ≈21 nm is obtained, whereas at 40 V it results as ≈168 nm; at the same time the tube diameter increases from 45 to 200 nm (Fig. 2a–d). From these data, a defined self-organized spacing of TiO_2 NTs is obtained in a limited voltage range 10–40 V; at lower voltages (e.g. 5 V) only a thin porous oxide is obtained and at higher voltages (>40 V) nanotubes do not grow uniformly over the surface

but anodization results in bundled tubes or the formation of a sponge-like oxide layer. This observation of a "region of existence" for spaced nanotube formation resembles findings reported for classic tubes (hexagonal packed) grown in EG, where with increasing voltage also first a transition from a nanoporous to a nanotubular morphology and at high voltages a transition to sponge-like oxide was observed [5,18, 19].

If the morphological data for outer diameter and spacings are evaluated, linear trendlines are obtained in the 10–40 V voltage range; at the higher end of the range, quite high errors for diameter and spacing occur, due to the strongly increasing inhomogeneity in morphology. I.e. due to the formation of a discontinuous nanotubular layer at high voltages, the errors are more evident for spacing due to the fact that overall the applied voltage has also a better control over the diameter of NTs.

A statistical evaluation of the dependence of number of nanotubes per unit area, as a function of voltage is plotted in Fig. 2e showing that in accord with increased spacing and tube diameter, a decrease of overall nanotube density is obtained.

Valuable insights can also be gained from the current density–time (J-t) plots (Fig. 2f). For voltages that lie within the "ordered spacing regime" (10–40 V), profiles present the typical regions encountered in nanotubes growth, i.e. the initial region where J is decreasing exponentially due to coverage of the anodized surface with a thin compact oxide film [6,20,21]. This is followed by a mild increase of J (usually ascribed to surface area increase due to initial porosification) and the third region, where a steady-state value is established (significantly higher than
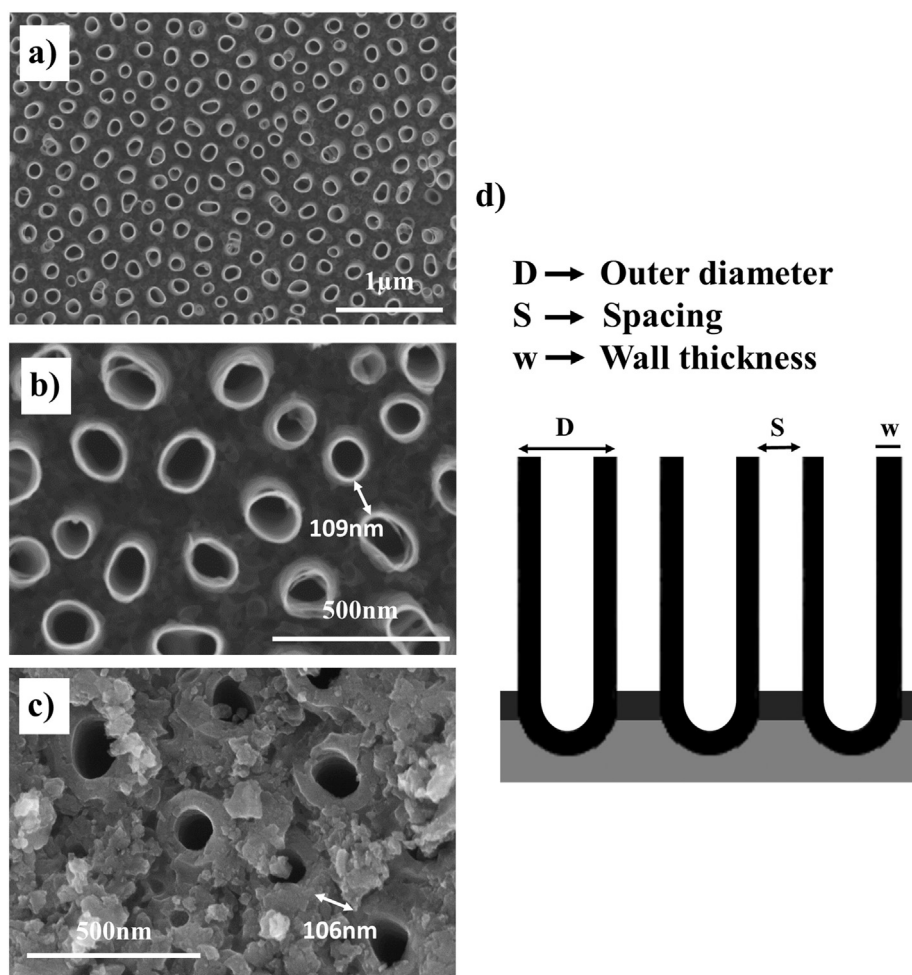

Fig. 1. Spaced TiO_2 nanotubes' morphology: a) and b) top view SEM images of spaced TiO_2 nanotubes and c) top view image of nanotubes cracked close to the bottom. Nanotubes are obtained at 30 V in DEG + 4 wt% HF + 0.3 wt% NH_4F + 1 wt% H_2O for 4 h. d) Schematic of spaced TiO_2 nanotubes showing the main morphological characteristic.