Fast growth of TiO₂ nanotube arrays with controlled tube spacing based on a self-ordering process at two different scales

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Abstract

In the present work, we introduce a technique to achieve rapid growth of self-ordered anodic nanotubes with a well-defined tube-to-tube spacing (spaced tubes) and single-wall morphology. By optimizing the anodization conditions (electrolyte, temperature, etc.), the growth rate of spaced tubes can be ≈ 25 times faster than in conventional approaches while maintaining a tube-to-tube spacing of ≈ 100 nm. We show that the origin of the tube-to-tube spacing is self-ordering of nanotubes on two different scales – the primary large tubes are embedded in a matrix of secondary, very short nanotubes with a small diameter. Preferential etching of the small tubes during anodic growth leaves behind an ordered array of spaced individual tubes with a well-defined tube-to-tube spacing.

Keyword: Anodization, TiO₂ nanotubes, Two-size scale, Fast-growth, DMSO

Link to the published article:

<https://www.sciencedirect.com/science/article/pii/S1388248117300681>

1. Introduction

Since the first reports on self-ordered nanotube or nanopore growth on Ti or Ti alloys through electrochemical anodization by Assefpour-Dezfuly et al. [1] and later by Zwilling et al. [2], Gong et al. [3] and Beranek et al. [4], TiO₂ nanotubes (NTs) have been explored for a wide range of applications and have become one of the most investigated nanostructures over the past decade [5].

A high level of control over morphological properties, such as diameter, length, wall thickness, wall structure, as well as over crystal phases (amorphous, anatase, rutile) has been achieved [5,6]. A range of morphological variations has been produced, including bamboo tubes, branched tubes, the fabrication of membranes, or single-walled TiO₂ NTs [6–9]. Usually, nanotubes grown in most organic electrolytes e.g. ethylene glycol (EG) or di-ethylene glycol (DEG), have a double-walled (DW) structure with a carbon-rich inner shell. However, tubes grown in di-methyl sulfoxide (DMSO) or after specific etching treatments show a single-walled (SW) morphology [10–12], which has been found to provide significantly better electrical properties [13] than double-walled tubes.

A feature observed in a number of anodization procedures is a slight increase in the tube diameter over anodization time, and thus some interspace at the tube tops can be established [14]. However, only a few experimental approaches report tube layers with a true and controllable inter-tube spacing over the entire tube length. One method of producing regular arrays of individual tubes with control over the tube-to-tube distance uses DEG electrolytes [15]. A second electrolyte class that can be used to achieve such spacing is DMSO [10]. In both cases, however, the tubes typically grow at rates of 0.2–0.3 $\mu\text{m/h}$ i.e. tens of hours of anodizing are needed to grow spaced tubes to a length of several μm [16–27].

Moreover, the origin of spaced tube growth remains unclear; in general, under “spaced tube conditions” it is observed that single tubes grow in a surrounding mesoporous oxide that is then

(due to its small feature size) etched faster than the tubes. This may be the reason for slow tube growth and correspondingly long exposure to the electrolyte i.e. to achieve preferential etching of the inter-tube material that leads to a morphology of separated individual tubes.

Here we demonstrate the rapid growth of spaced TiO_2 nanotube films, as illustrated in Figure 1(a), by tailoring the electrochemical conditions (electrolyte composition, voltage and temperature). The growth rate of spaced nanotubes in DMSO-based electrolytes is drastically accelerated (a length of $\approx 3\mu\text{m}$ is obtained in 10 min). This is achieved by anodization near anodic breakdown without losing the tube-to-tube spacing under these conditions. Furthermore, we show that the growth of spaced tubes is based on self-organisation at two different scales, with the intertube matrix consisting of short, small-diameter NTs of nm dimensions that are etched preferentially.

2. Experimental

The synthesis of spaced NTs includes a two-step anodization process. In the first step, a 0.1 mm Ti foil (99.6% pure tempered annealed, ADVENT) was anodized in EG + 0.5 wt% NH_4F + 2M H_2O at 80 V for 10 min and the nanotube layer was removed using ultrasonication in distilled water. This treatment does not influence the self-ordering of NTs at two different scales, but it improves the uniformity of the NTs and the steady state is reached faster than with other pre-treatment techniques. In the second step, spaced TiO_2 NTs were formed in an electrolyte that consists of dimethyl sulfoxide (DMSO) or di-ethylene glycol (DEG) with additions of 4 wt% HF (40 % Sigma Aldrich), 1 wt% H_2O , and 0.3 wt% NH_4F (note that we do not consider the water from HF (40% HF), and 1 wt% H_2O addition is indicated). After anodization, the samples were immersed in ethanol overnight and dried in a N_2 stream. Anodization was carried out in a two-electrode configuration with Pt as cathode and the Ti substrate as anode (1.5 cm inter-electrode distance in 30 ml electrolyte), at 10–50 V and the

temperature of the substrates was varied from 10 to 50°C (the temperature of the back of the substrates was controlled with a thermostat).

To crystallize the TiO₂ structures, the samples were annealed at 450°C for 1 h in air with heating/cooling rates of 30°C/min using a Jetfirst Rapid Thermoannealer (RTA, Jipelec, France).

The morphology of the NTs was investigated using a field-emission scanning electron microscope (FE-SEM S4800 Hitachi) equipped with an energy dispersive X-ray (EDX) analyzer. The crystallinity of the NTs was analyzed by X-ray diffraction (XRD, X'pert PhilipsMPD with a Panalytical X'celerator detector, Germany) using graphite monochromized Cu K α radiation (wavelength 1.54056 Å). XPS measurements were conducted on a high-resolution X-ray photoelectron spectrometer (PHI 5600) using monochromatic Al K α radiation (1486.6 eV, 300 W) for excitation (peaks shifted with C1s 284.8 eV).

3. Results and discussion

The present investigations were conducted in a DMSO electrolyte containing 0.3 wt% NH₄F + 1 wt% H₂O + 4 wt% HF. The typical features of the resulting morphology are shown in Figure 1. Figures 1(b–f) show a spaced nanotube structure obtained at 30 V for 1 h (at 30°C). These nanotube layers have a clear morphological difference to classic anodic nanotubes, which usually grow in a close-packed arrangement. The arrays in Figure 1 show a distinct space between individual nanotubes from top to bottom (as evident from the top-view SEM image shown in Figure 1(b), and the cross-section view in Figure 1(d)). Only at the bottom, as seen from the bottom-view SEM image (Figure 1c), is the space between the NTs filled with a second morphology. Zooming in on this intertube matrix (Figure 1(e–f)) reveals that it is composed of very short NTs of small diameter. Such a morphology can be caused by rapid repetition of tube

initiation and branching events. In this arrangement, the small nanotubes follow a particular order (see Figures 1(a) and 1(e–f)). Sequential stacking of small nanotubes can be observed that split after short growth (e.g. one small nanotube into two small nanotubes) in a direction perpendicular to the substrate (highlighted in Figures 1(a) and 1(f), with a stack width (lateral) of 105 ± 20 nm). The growth of small and large NTs is a continuous process. The small NTs have a much thinner morphology that makes them more vulnerable to etching. Thus, the packing density between the main growing NTs is higher close to the bottom of the layer; in the upper part of the layer the small NTs have been fully etched (have vanished).

To evaluate the impact of the optimized electrolyte [15] on nanotube growth, we performed systematic investigations in a DMSO electrolyte containing 4 wt% HF, 1 wt% H₂O and 0.3 wt% NH₄F while varying the voltage and temperature. The slow-growing NTs (initial conditions) were fabricated in a DMSO electrolyte containing 2 wt% HF at 30 V (at 30°C) for 1 h. Typical current density–time (J–t) curves are shown for two cases (initial conditions and after optimization) in Figure 2(a). For fast-growing NTs, a steady-state is established at a higher J value (≈ 1.9 mA/cm²) than for the slow-growing NTs (≈ 0.6 mA/cm²). Although the growth efficiency is higher for the initial conditions (≈ 0.55 μm/C) than for the optimized conditions (≈ 0.43 μm/C), the initial layer has a porous structure and requires longer anodization to complete the self-organization process. Note that anodization was also performed at higher voltages (≥ 50 V) and higher temperatures ($\geq 50^\circ\text{C}$), but these conditions did not lead to longer nanotubes.

Figure 2(b) shows the plot of geometrical features versus voltage and the images of the resulting nanotube layers in the optimized DMSO electrolyte. The outer diameter and thickness increase with increasing voltage: at 10 V nanotubes ≈ 870 nm long (outer diameter, 45 ± 5 nm) are produced while at 30 V nanotubes ≈ 3.2 μm long (outer diameter, 118 ± 8.5 nm) are obtained (see also Figure 2(b)). Anodization at higher voltages disrupts the self-organization and leads

only to spongy oxide formation. The transition from self-organized NTs to spongy oxide starts at voltages higher than 30 V and at 50 V only non-ordered oxide is formed. These findings indicate that, in line with the literature [15], spaced nanotubes formed in DMSO are grown in a transition state between (i) self-organized tubes and (ii) a secondary oxide (SO) morphology (here we show that this SO is composed of small NTs), and that the voltage controls the transition between these two morphologies. We find that 10–30 V represents the optimal working range for this electrolyte (Figure 2(b)).

A key factor in controlling the morphology is the temperature, and therefore we evaluated anodization at 30 V (the optimal voltage) at different temperatures between 10 and 50°C (Figure 2c). While anodization temperatures $\leq 20^\circ\text{C}$ lead to non-ideal NTs (non-ordered small nanotube morphology), anodization at 30°C results in spaced nanotubes. Note that anodization at high temperatures preferentially etches the small nanotubes and reduces the tube-to-tube spacing while increasing the nanotube density. Therefore, the temperature of the substrate has a decisive role on the growth rate of the NTs and on the organization of the NTs at two different scales, since the tube-to-tube spacing is established by the stacks of small NTs. We established an optimal working voltage (30 V) and anodization temperature (50°C) by systematic screening of the anodization parameters. Normally, an increase in electrolyte temperature increases the conductivity of electrolyte, and decreases the anodizing breakdown voltage. The threshold voltage for breakdown depends on the ionic species in the electrolyte. DMSO is a dipolar aprotic solvent [28,29]; due to its protophilic nature, DMSO accepts the hydrogen (proton) from HF, and increases the electrolyte pH. This effect diminishes the chemical etching power of the electrolyte and is able to shift the breakdown voltage.

Anodization at 50°C shows that at the initial stage, the growth rate is the highest and with increasing time the dissolution/etching rate at the top equilibrates with the growth rate at the oxide/metal interface.

Figure 2(d) compares the current results with reported studies for DMSO [18–26]. It can be seen that by using the parameters of the present work, very fast growth can be achieved ($\approx 3\mu\text{m}$ in 10min). It should be noted that the growth rates reported here for DMSO spaced nanotubes under optimized conditions are approximately 25 times higher ($\approx 9\mu\text{m/h}$) than those reported previously, including previous observations for DEG NTs (Figure 2(d)) [15].

The above findings suggest that ordered, spaced NTs form in a limited voltage range in both DEG [15] and DMSO electrolytes. Despite the similarities in the morphology, DEG and DMSO spaced NTs have a different wall structure and chemical composition. Figure 3(a–b) illustrates the single-walled structure of spaced NTs grown in DMSO and the double-walled structure of spaced NTs grown in DEG. XPS and EDX analysis of DMSO and DEG NTs (Figure 3(c)) confirm the lower carbon content of NTs grown in DMSO and higher carbon content for NTs grown in DEG, the latter having a carbon-rich inner shell [10]. In XPS, with a resolution depth of $\approx 3\text{--}10\text{ nm}$, a slightly higher fluoride content is observed for DMSO nanotubes (due to etching of the top of the nanotube by the fluoride ions), while a similar amount of fluoride is detected by EDX in both DMSO and DEG NTs.

Yoriya et al. [30] and Liu et al. [13] report on partial crystallization of slow-growing NTs in DEG and EG-DMSO mixed electrolytes (anodization times of 3 days [13] and 48 h [30]). Here, using a higher growth rate, no crystallization of the nanotubes is observed after growth. Figure 3(d) shows the XRD data for the as-formed and annealed DMSO and DEG NTs, and clearly reveals that the as-formed NTs are amorphous but can be converted to anatase by annealing.

Although similar parameters (ionic strength of the electrolyte and anodization parameters) have been used for anodization in both electrolytes, anodization in DMSO leads to the formation of $\approx 3.2\mu\text{m}$ long NTs in 1 h, whereas for DEG electrolytes 4 h of anodization are needed to produce a comparable structure ($\approx 1.2\mu\text{m}$), see Figure 3(e). In other words, nanotubes

grow more efficiently in DMSO electrolytes as less charge ($\approx 2.3\text{C}/\mu\text{m}$) is needed to grow a certain length of tube compared with DEG electrolytes ($\approx 31\text{C}/\mu\text{m}$).

Like DMSO NTs, DEG NTs show a well-defined spacing and the formation of small diameter nanotube [10] stacks between the larger tubes (see Figure 3(e)). Tsuchiya et al. [31–33] have reported on the self-organization at two scales that can occur for tube growth on various Ti alloys. The present work shows a similar effect but on pure titanium, where the length of the small NTs is limited to only several tens of nanometers. The cross-section SEM images of DEG spaced NTs in Figure 3(f–g) (above – ion-milled cross-section, below – normal cross-section) show that the small NTs are connected with each other and with the spaced NTs by ripples. Such ripple formation is usually connected with the water content of the electrolyte [34] or can be induced by a voltage pulse [35]. Here ripple formation as well as branching of the tubes must be ascribed to self-induced effects based on voltage ($\geq 30\text{ V}$) and electrolyte composition (DMSO, DEG with HF and H_2O content) and their variations over time.

4. Conclusions

The present work reports on an approach to achieve fast growth of spaced TiO_2 nanotubes in DMSO electrolytes. We show that the key factors for fast growth of spaced nanotubes are the applied voltage and the anodization temperature. The spaced nanotubes grow as a consequence of a self-organization process at two scales, with small NTs stacks filling the space between larger NTs. Anodization parameters influence this process, as under our optimized conditions a higher growth rate and improved self-organization are attained. In other words, not only fast growth but also strongly improved homogenous ordering can be achieved.

Acknowledgements

The authors acknowledge the ERC, the DFG, the DFG “Engineering of Advanced Materials” cluster of excellence and DFG “funCOS” as well as Toyota Motor Europe (TME) for financial support.

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Figure captions

1 h at 30°C (in DMSO + 4 wt% HF + 1 wt% H₂O + 0.3 wt% NH₄F). (e) Ion-milled and (f) normal cross-section SEM images of spaced nanotubes showing the organization of small and large nanotubes.

Figure 2 (a) Comparison of current density–time (J–t) profiles for 1 h anodization at 30 V (30°C) under the initial conditions (DMSO + 2 wt% HF) and after optimization (DMSO + 4 wt% HF + 1 wt% H₂O + 0.3 wt% NH₄F). Variation of geometrical features (outer diameter, spacing and length) in optimized DMSO electrolyte as a function of (b) voltage (at room temperature, insets show the top SEM images of resulting structures at 5, 30 and 50 V) and (c) temperature (at 30 V). (d) The length versus time plot showing the literature overview of DMSO electrolyte and our observations for optimized DMSO and DEG electrolytes. Lines are guides to the eye only.

Figure 3 Top view of nanotubes cracked close to the bottom of (a) single-wall DMSO and (b) double-wall DEG nanotubes. (c) XPS and EDX analysis for DMSO and DEG nanotubes showing fluoride (F) and carbon (C) content. (d) XRD analysis for as-formed, annealed DMSO and DEG nanotubes. (e) Cross-section (inset showing the bottom view) SEM images of nanotubes obtained at 30 V for 4 h at 30°C in DEG + 4 wt% HF + 1 wt% H₂O + 0.3 wt% NH₄F electrolyte. (f) Ion-milled and (g) normal cross-section SEM images of nanotubes illustrating

the organization of small and large nanotubes (obtained in DEG + 1 wt% HF + 1 wt% H₂O + 0.3 wt% NH₄F).