Critical parameters and factors in the formation of spaced TiO₂ nanotubes by self-organizing anodization

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Abstract

Self-organized TiO₂ nanotube arrays can be grown under a wide range of electrochemical conditions. In the present work, we evaluate the occurrence of spacing between tubes and the connection of this effect to organization of tubes on two-size scales. The results show that tube-spacing is initiated in the very early stages of anodization between individual pore morphologies. Furthermore, the spacing, as well as the organization on two-size scales can be controlled by changing the anodization conditions, e.g., electrolyte composition, applied voltage and temperature. Namely, adjustment of H₂O content, electrode temperature and voltage can lead to spaced nanotubes, and allow to control spacing. Finally, we draw conclusions on possible mechanism relevant to the growth of spaced tubes.

Keyword: Anodization, TiO₂ nanotubes, Two-size scale, Spaced nanotubes

Link to the published article:

<https://www.sciencedirect.com/science/article/pii/S0013468618304249>

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 broad range of applications and have become one of the most investigated nanostructures over the past decade [5].

Meanwhile, a high level of control over morphological features, 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 [5,7–10].

Generally, self-ordered TiO₂ nanotube arrays grow in a hexagonally close-packed (CP) configuration, i.e., have no or only very narrow tube-to-tube spacing (top spacing). However, previous research shows that with certain electrolyte compositions, spaced NTs, i.e., showing regular gaps between individual tubes, are obtained [11–14]. This particularly if the electrolyte contains diethylene glycol (DEG) or dimethyl sulfoxide (DMSO) organic solvents in addition to HF and H₂O. Over the years, few more electrolytes, e.g., ethylene glycol (EG), tri(tetra, poly)-ethylene glycol, were reported to result in the growth of spaced or “loose-packed” NTs under specific anodization conditions [15,16].

In our previous work, we showed that the growth of spaced tube is based on self-organization on two scales, with the inter-tube matrix consisting of short, small-diameter NTs of nm dimensions that are etched-off preferentially leaving regularly arranged large diameter tubes behind [17]. Thus, the special characteristic of spaced tubular layers is self-organization on two different scales. In other words, large single tubes grow in a surrounding mesoporous oxide (or small nanotubes stacks) that is then (due to its small feature size) etched faster than the large tubes [17]. Note that the organization on two different scales as well as the “space tube region” is determined by the anodization parameters, e.g., applied voltage, applied temperature and electrolyte composition [13,17–19].

This observation of a “region of existence” resembles the reported findings by Albu et al. [20] for classic close-packed tubes (hexagonal packed) grown in ethylene glycol (EG), or in aqueous electrolytes reported by Tsuchiya et al. [21], which indicate that a first transition from a nanoporous to a nanotubular morphology with increasing voltage occurs, followed by a transition to sponge-like oxide at even higher voltages. Similarly, Mor et al. [22] reported a metastable condition for close-packed NTs obtained in 0.5% HF containing aqueous electrolyte

by changing the voltage. Other observations indicate that transition from one morphology to the other, can also occur at constant voltage, i.e., minor changes in water content in ethylene glycol electrolyte [23] or change in sweep rate in aqueous electrolyte [24] drives the transition from porous oxide to tubular morphology or from tubular morphology to sponge oxide. However, in the case of spaced nanotubes transition from tubular structure to sponge oxide occurs gradually [18].

A large amount of research has been dedicated to understand the mechanistic aspects of self-organization, and some recent works can be summarized. Thompson et al. [25] and Hebert et al. [26] proposed a plastic-flow model of the oxide as a consequence of compressive stress. Moreover, recent studies show that pores initiate because of morphological instability of the initial oxide surface [27–29]. Later, Hebert et al. [30] suggested a quantitative model, according to this model, the morphological instabilities (stabilization of instabilities) lead to the formation of self-ordered oxide layers. In addition to the works above mentioned, there is an intensive research on electrode reaction kinetics to explain the mechanism of self-organized pore/tube formation [31,32].

In the present work, we describe the establishment of spacing as well as the self-organization on two-size scales in the early stages of tube growth. Moreover, we present an overview of critical parameters that lead to spaced tube growth, to the occurrence of an organization on two-size scales and discuss the mechanistic model based on experimental findings.

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 0.5 wt% NH_4F , 3.6 wt% H_2O , containing ethylene glycol (EG) electrolyte at 80 V for 10 min, and then the nanotube layer was removed by ultrasonication in distilled water. In the second step, spaced TiO_2 NTs were fabricated in diethylene glycol (DEG) or dimethyl sulfoxide (DMSO) with additions of 4 wt% HF (40 %), 7 wt% H_2O , and 0.3 wt% NH_4F . The composition of electrolyte was investigated for DEG based electrolyte, i.e. the water content was varied from 6 to 26 wt% and HF content from 0 to 4 wt% in the electrolyte. After anodization, the samples were immersed in ethanol overnight and dried in a N_2 stream. Anodization was conducted by means of a 2-electrode set-up (Pt as a cathode, and the Ti substrate as an anode (~1.5 cm inter-electrode distance) in ~30 ml electrolyte) at a voltage range between 10–60 V and the electrode temperature was adjusted using a thermostatically regulated back-plate (Huber, cooling-heating

circulator) to the sample – this was found most effective to control the sample temperature. The temperature of the Ti substrate/electrode was adjusted from 10 to 60 °C. Previous reports show that convection conditions have an influence on the resulting morphology [33,34]. Based on that, we investigated the effect of stirring on spaced tube formation and we found that stirring disturbs the nanotube formation (i.e., either shortens the length or totally etches the tubular layer) depending on the speed/rotation rate. Considering these preliminary findings, anodization was performed under natural convection conditions.

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. In this study, all the geometrical features were measured from SEM images using the Image J software and the values are the average of at least 15 measurements. To note that when showing morphological features data, dashed line are only guide to the eye while solid lines are fitted.

XPS measurements were performed 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). Sputter depth profiles were obtained by Ar⁺ sputtering with a sputter rate of 2.2 nm/min.

3. Results and discussion

In this study, we systematically evaluate the growth of oxide from the very early stage of anodization to follow the space initiation between the individual nanotubes and growth of tubes, as well as the influence of a wide range of anodization conditions on spaced tube morphology and the organization on two-size scales.

3.1 Growth sequence

The spaced tubular layers were produced in HF, NH₄F, and H₂O containing DEG electrolyte. Figure 1a shows a 3D drawing of the spaced nanotube formation stages that contain nanoscopic pore initiation (this becomes evident in SEM after 30–120 s), the formation of hemispherical-like oxide structure under channel-like initiation layer (after 300 s) and the nanotube formation (starting after 480 s). The related current density-time profile with the indication for each stage and the corresponding SEM images of the resulting oxide layer are shown in Figure 1b and c.

The current density-time profile of spaced tube formation shows a similar trend as for the close-packed NTs: first, it shows an exponential decrease. The exponential decrease of current

density illustrates the fast growth and thickening of the oxide layer, in line with literature [31]. Later, a steady state is established after 1800 s of anodization (Figure 1b) where the oxide formation and dissolution in the F-ion containing electrolyte are equilibrated. In this stage, the growth rate of the oxide reaches a saturation.

Figure 1c shows high magnification SEM images of the resulting layers for each growth stage. In the pre-anodization step, dimples with ~120 nm inter-dimple distance are obtained, and after 30 s anodization of the pre-treated substrate, the Ti surface is covered with shallower nanoscopic pores (inside the big dimples) accompanying a ~30–40 nm inter-pore spacing. With increasing time, the shallower pores grow even deeper in the compact passivation/oxide layer to form nanochannels (as an initiation layer). One can observe that not all of the shallow pores evolve into channels, instead, some of them merge to form channels with bigger openings.

Each channel acts as a starting point for pore initiation and later to a hemispherical-like oxide structure. It is worth mentioning that in the early stage of spaced tube growth (300 s) the hemispherical-like geometries (initiated in the nanochannels) show already spacing between them as illustrated in Figure 1 300 s (see also inset, A and B). We believe that first, distinct initiation sites (such as crack-like) form throughout the oxide layer, as opposed to close-packed nanotubes where the initial oxide layer does not show the formation of distinct initiation sites [35].

The initial oxide morphology shows differences in growth rate from region to region, namely, we observe brighter and darker regions. In the brighter region, the remaining from the initial channel layer (needle-like tube walls in the cell junction, Figure 1c 300 s A), whereas in the darker area nano hemispherical-like initiation sites, which are the early stages of spaced NTs are observed (with an oxide layer thickness of 22 ± 2 nm and the inter-distance between nano-hemispheres is around ~60–70 nm) — Figure 1c 300 s, B. This difference may be due to the substrate grain orientation effect, for example literature reports that the growth of the oxide layer and its features depend on, e.g., grain orientation, disorder, defects, pre-treatment, and can change from grain to grain, this leads to different film growth rates and consequently different oxide thicknesses on different grains [36–40]. For the anodic oxide layers, under mild anodization conditions some grain influence on appearance has been observed under EBSD [36,41,42], however in these conditions we could not see a distinct difference.

In 300 s, the hemispherical-like structures show a uniform size distribution (Figure 1c for 300 s), with increasing time, i.e., 480 s the difference in size is more pronounced (as shown in Figure 1c for 480 s). These hemispherical-like oxide structures gradually evolve into a circular tubular array with time. In this stage, the organization of tubes on two-size scales becomes

visible — big-diameter nanotubes are surrounded by small-diameter nanotubes [12,17]. Note that the spacing (after 480 s) in between big-diameter NTs is not the final one (i.e., for 4 h anodization), and is approximately one-third of it, see previous report [18]. In this organization, small- and big-diameter nanotubes are connected with each other by ripples and a compact-like oxide layer underneath.

In the 4th and last stage of growth (≥ 900 s), the features of big-diameter nanotubes (i.e., diameter, wall thickness, and length) reach an average length of ~ 270 nm and a diameter of ~ 90 nm, the diameter of small nanotubes is ~ 40 – 60 nm (Figure 1c, 1800 s). During 3rd and 4th stages, the spacing is further changed: most likely some of the nanotubes stop growing, and surrounding nanotubes will accordingly enlarge their diameter. Yasuda et al. [43] proposed that big pores, due to higher individual current flow, produce a higher amount of H^+ ions that increases the chemical etching and so the pore bottom etches deeper, on the other hand, small pores that produce a low amount of H^+ will become smaller and smaller. Note the fact that small-diameter NTs have a thinner morphology and a weaker connection with the Ti substrate compared with large diameter NTs, but they are tightly connected with each other and with the large diameter NTs by ripples, like a network [17].

XPS depth profiling analysis was conducted to evaluate the composition of the oxide layer at different growth stages, see Figure 2. The results suggest that F-ion incorporation to the oxide layer (F1s at 684–685.5 eV) is visible from the early stage of growth and fluoride is accumulated at the oxide/metal interface (Figure 2a–c). According to the XPS profiles for the different growth stages, the interface has been reached for 120 s anodization at ~ 8 – 9 nm, for 5 min anodization at ~ 9 nm and for 30 min anodization at ~ 80 nm. (The layer thickness for 30 min anodization varies from ~ 100 to ~ 470 nm). The difference between the layer thicknesses measured from SEM and XPS depth profiling is due to the high roughness of the substrate, non-uniform thickening (due to grain effects) as mentioned in the previous section and non-uniform sputtering of the oxide layer.

From a depth profiling for ~ 1.2 μm long spaced NTs, we observed that nanotubes have an even distribution of Ti, F and O elements at the top, i.e., in the first ~ 200 nm, as illustrated in Figure 2d. Additionally, only the top most layers contain carbon (adventitious C peak at 284.8 eV, and C-O or C=O at ~ 286 and 288.5 eV, respectively) as with sputtering the C content decreases drastically (it is worth mentioning that DEG NTs are single-walled at the top and double-walled at the bottom [17] different from the double-walled EG NTs [44]). In line with the literature, F-ion containing species are incorporated from the solution to the films throughout their thickness and are enriched at the oxide/metal interface [44].

3.2 Influence of voltage

One of the key factor controlling the morphological features of NTs is the applied voltage. Figure 3a and b show the arrangement on two-size scales, i.e., big-diameter NTs are embedded in small-diameter tube stacks. In this two-size scale arrangement, when small-diameter nanotubes grow, they follow a particular orientation: a sequential stacking of small nanotubes [17], with a changing stack width depending on the anodization condition. The small-diameter NTs appear to be formed as a result of a rapid repetition of tube initiation and branching events.

The evaluation of spaced TiO₂ NTs during anodic oxidation is accompanied by the formation of large number of terminated small NTs. The formation of small NTs is continuous and fast process; termination of small pore and formation new one in the tube front. In literature, fast growth of short channels/pores is attributed to diffusion control of electrochemical reaction, i.e. the growth rate of pores depends on the gradient of the electrolyte concentration at the pore bases, consequently growth rate is self-adjusting; short, branched pores show fast growth and tendency to terminate, on the other hand, deeper pores display slow growth rate [32].

The bottom of small- and big-diameter NTs has a “brain morphology like” structure, see Figure 3b. The reason why such a “brain morphology like” structure forms still is not clearly understood, but this morphology resembles the pattern formation that is observed in reaction-diffusion situations (Turing patterns) [45], or spinodal decomposition situation [5], or may originate from oxide flow phenomena [26,30].

The graph in Figure 3c displays the linear dependence of outer diameter of big- and small-NTs on the applied voltage. In literature, the tube diameter is reported to be linearly dependent on the applied voltage according to a $D=k \times V$ relation [6,46–48], where k is equal to $2 f_g$ (f_g being the growth factor for anodic oxides), D is tube diameter and V is the applied voltage. The variation of the calculated growth factors for small- and big-diameter NTs using the above equation as a function of the applied voltage (Figure 3d) follows a similar trend: while the average growth factor for big-diameter NTs is ~ 2.5 nm/V, in the case of the small ones, it is ~ 0.8 nm/V (IR-drop is not considered). Note that the growth factors were also calculated for small and big diameter NTs by considering the solution IR-drop (or using effective/cell voltage), following literature [6,49]. In our case, only minor differences between the growth factors (for small- and big-diameter NTs) with and without IR-drop are observed. Therefore, the IR-drop effect was not further taken into account in this work. A small-diameter tube growth is explained by the fact that the neighboring NTs limit the expansion and the growth of the outer diameter of the center NTs [50,51]; therefore, the growth factor for small-diameter NTs is lower

than the reported value for TiO_2 , $\sim 2\text{--}3\text{ nm/V}$ when a 2-electrode [52] or a 3-electrode [43,53–55] set-up was used.

We evaluated spaced tube formation in different organics (DEG, DMSO) with different compositions and in all cases spaced NTs grow with a similar trend, i.e., low voltage - porous oxide, moderate voltage - tubular layer and high voltage - only sponge oxide (no vertically aligned spaced NTs) formation. In line with literature, self-organized array formation is observed in a narrow voltage range [20–22], which for this study is limited between 10–40 V. Outside of this voltage range, for instance, anodization at high voltages (at 42 V) leads to discontinuous/isolated nanotubular layer patches embedded in a dense, sponge oxide layer (small tube stacks), see Figure 3e–h. In addition, anodization at 42 V induces branch formation, non-uniform thickening of barrier layer (tubes with bigger diameter), and an increase in the amount of sponge oxide. Similar abnormalities in tubular layers are observed by other researchers [56–59]. Normally, branch-like structures are reported to be formed if a sudden change in electrical field takes place, which is triggered by temperature, electrolyte or voltage variation during anodization [50,60–62]. As an exception, branch-like formation was reported at constant anodization voltage by *i)* Mohammadpour et al. [63], and by *ii)* Chen et al. [15] for spaced NTs.

Figure 3f shows the dimples of spaced nanotubes and sponge oxide layer (that actually consists of small-diameter tubes). Apparently, the tube and sponge oxide dimples show clear difference, i.e., while tube dimples go deeper into the Ti, for sponge oxide the dimples are less clear. This is attributed to the fact that small-diameter NTs grow in the area where tube nucleation has not occurred [64], under a continuous growth and dissolution state (e.g., the rapid repetition of branching). Therefore, small-diameter NTs have thinner morphology (thin barrier layer), and this makes them more susceptible to chemical etching. Consequently, the packing density between the main growing NTs is higher in the lower part of tubes (tube front), while in the upper part of the tubular layer the small NTs have been fully etched (have vanished) [17] that generates defined tube-to-tube spacing at the top.

Also, we observed that the thickness of the barrier layer of small-diameter and big-diameter NTs is not similar; for instance, at 30 V the barrier layer of small- and big-diameter NTs is ~ 36 and $\sim 53\text{ nm}$, respectively. At high voltage (42 V) the difference is more pronounced, i.e., the barrier layer of big-diameter nanotubes is $\sim 90\text{ nm}$ (Figure 3g, 42 V) and for small-diameter NTs is around $\sim 30\text{ nm}$ (Figure 3h, 42 V). Generally, a non-uniform thickening of the barrier layer is ascribed to the non-uniform current distribution as a result of the structural effects or defects in the metal or oxide [65]. The different thickening of the barrier layer leads to an uneven field

distribution that causes non-uniform dissolution rates, e.g., a thicker oxide leads to slower ion migration and thinner oxide induces faster migration [43,46,66]. This illustrates the fact that the pore bottom of small-diameter NTs is thinned down sufficiently to continue growth under lower field conditions, in line with literature [6,67].

3.3 Influence of anodization temperature

To have better control over electrode temperature and to maintain uniform temperature distribution throughout the anodized substrate, anodization was performed under applied-electrode temperature (controlled-electrode temperature, as mentioned in experimental section).

Figure 4 presents the temperature influence on the uniformity of spaced nanotubular layers. The findings show that the controlling the temperature of the Ti substrate remarkably affects the morphology of nanotubes; namely, anodization without temperature control leads to a local tube formation (differences from region to region), whereas anodization at 30 °C improves the uniformity of the tubular layer, i.e., NTs are uniformly spread on the Ti substrate, as illustrated in Figure 4a and b. Another significant finding is that, while the tubular layer fabricated without temperature control (uncontrolled-electrode temperature) has a high density of small-diameter nanotubes (sponge-stacks), NTs produced at 30 °C have an overall uniform tube density except for the very thin layer of sponge oxide at the tube bottom. The high sponge density (when the electrode temperature is not controlled) is likely due to intrinsic heat generation (Joule heating due to high current density or high electrical field) that might induce a local sponge oxide growth, which is attributed to an increased growth rate. In literature, sponge oxide is reported under accelerated growth rates, for instance under different high/breakdown voltages or under different thermal and hydrodynamic conditions [20,34,68].

In the present work, we observed an improved self-organization at 30 °C. This improvement can be ascribed to the heating effect. Briefly, electrode heating might influence the temperature of the electrolyte that is close to the electrode [69] that will affect the properties of electrolyte such as pH, conductivity, and viscosity. We measured electrode and electrolyte temperature simultaneously during anodization (under controlled-electrode temperature) using a contact and non-contact infrared thermometer, and we observed that while the electrode temperature does not change much, the electrolyte temperature increases during anodization.

Figure 4c shows the comparison of the current density-time profiles for anodization under uncontrolled- and controlled-electrode temperature (at 30 °C). The growth efficiencies were calculated for both conditions (the ratio between length and consumed charge during

anodization, and is calculated according to following equation: Growth efficiency=Length/Total charge). It yields for 30 °C a slightly higher growth efficiency (0.032 $\mu\text{m}/\text{C}$) than anodization without temperature control (0.029 $\mu\text{m}/\text{C}$). Controlling the electrode temperature not only changes the growth efficiency but also the outer diameter, and the tube spacing of NTs: 108 ± 14 nm, 185 ± 74 nm and 148 ± 21 nm, 109 ± 47 nm for anodization uncontrolled- and controlled-electrode temperature (30 °C), respectively (Figure 4a and b). The decrease in spacing with increasing anodization temperature is due to the fact that the longitudinal thickness of small-diameter tube stacks (sponge stacks) decreases from 151 ± 52 nm (without temperature control) to 80 ± 35 nm (30 °C), which results in a higher tube density (we considered only big-diameter NTs). The increase in electrode temperature to moderate values (i.e., $\leq 30^\circ\text{C}$) increases the outer diameter and spacing as well as the amount of sponge oxide, thus leading to higher tube density (considered only big-diameter NTs). Accordingly, the length of NTs reduces from ~ 1.7 μm to ~ 1.2 μm when the temperature of the electrode is adjusted to 30 °C.

We have performed additional experiments under constant charge for different anodization temperature and different HF content (data not shown). Anodization under constant charge does not lead longer spaced NTs, instead extension of the anodization time enhances the energy consumption without yielding longer nanotubes. Therefore, we believe that comparison of the length of tubular layer for fixed time is a more straightforward approach.

Above findings suggest that temperature has an influence on the morphology and the self-organization process of spaced NTs. Based on these findings, we investigated the influence of temperature in more detail and controlled the electrode temperature from 10 to 60 °C. From Figure 4d, one can see that anodization at low temperature (e.g., 10 °C) induces the formation of discrete nanotubes, embedded in a sponge oxide (small tube stacks with ~ 462 nm thickness). The increase in temperature reduces the size of small-diameter NTs or eliminates the sponge oxide (at e.g., 30 or 60 °C, see Figure 4e and f), as the amount of small NTs observed is dependent on the chemical dissolution of the oxide [17,64]. Thus, anodization at high-temperature, e.g. 50–60 °C, leads to sponge oxide free, shorter NTs with a defined spacing. However, one of the functions of these small-diameter nanotubes is to provide support for the big-diameter nanotubes and to keep the nanotubes standing together with a compact-like oxide (see inset in Figure 1c 480 or 900 s). When these small-diameter nanotubes are fully etched, and the compact-like oxide (consisting of fluoride-rich layer) is thinned, the over-etched big-diameter nanotubes partially collapse, see Figure 4f.

Figure 4g shows the current density-time profiles for different anodization temperatures. According to the J-t profiles, the steady-state current density increases with temperature (when the electrode temperature is controlled), e.g. the current density is 0.9 mA/cm² at 10 °C and 7.3 mA/cm² at 60 °C, however, the current density recorded without temperature controller reaches higher values (9.6 mA/cm²) than the one recorded at 60 °C, see Figure 4c and g.

The variation of geometrical features as a function of the anodization temperature is displayed in Figure 4g and i. Anodization temperatures influences significantly the resulting geometrical features of NTs. I.e., the outer diameter of NTs increases up to ≤ 30 °C (124 nm at 20 °C, 148 ± 21 nm at 30 °C), while at higher temperatures the outer diameter decreases (111 ± 12 nm at 60 °C). On the other hand, only minor variations are observed in the diameter of small nanotubes with varying the anodization temperature (< 50 °C). The above results suggest that the geometrical features such as diameter, tube-to-tube spacing, and inter-tube distance (i.e., distance between pore/tube centers) are correlated with the number of nanotubes per cm², as anodization at temperatures higher than 30 °C decreases the tube-to-tube spacing by increasing the number of tube nucleation sites. Moreover, anodization at a high temperature keeps the two-size scale organization, but the small-diameter tubes with thin barrier layer are mostly etched.

Overall, we observed that controlling the electrode temperature improves the uniformity and shortens time required for the self-organization process compared with long anodization times reported in the past for DEG nanotubes [12,13,70].

3.4 Influence of time

It is well-known that the morphology, especially the homogeneity or the degree of self-organization of NTs can be improved with anodization time [46]. In order to study the influence of time on the morphology of spaced nanotubes, anodization duration was varied from 30 min to 24 h.

Figure 5a–b displays SEM images of the tubular layers obtained by anodization for 30 min and 24 h. The nanotubes obtained for 30 min anodization have dense small tube stacks in the lower part of tubular layer, which leads to a larger tube-to-tube spacing (Figure 5a), whereas longer anodization time results in uniform and larger NTs with less tube-to-tube spacing. The variation of geometrical features of spaced NTs as a function of anodization time is summarized in Figure 5c. The enlargement of the tube diameter with time is more pronounced than changes in other geometrical features; for instance, the outer diameter of NTs is ~ 103 nm for 30 min, and it reaches ~ 168 nm for 8 h anodization, and only a further increase by 8–10 nm is observed

for 24 h anodization. While the diameter of NTs stabilizes after 8 h, the spacing reaches a plateau after only 4 h anodization: the top spacing for 30 min, 4 h, and 24 h anodization are 113 ± 40 nm, 109 ± 47 nm, and 106 ± 21 nm, respectively. Similarly, the wall thickness shows a decreasing trend after 4 h anodization, i.e., the wall thickness for 30 min anodization is 12 ± 2 nm, for 3 h anodization it is 19 ± 3 nm, and for 24 h anodization it is 13 ± 2 nm. The speed of the chemical etching of the tube walls/tube tops depends on the electrolyte composition and anodization parameters (e.g., water content, the fluoride content, the acidity of the electrolyte, and applied voltage/temperature), which have decisive influence on the properties of the electrolyte (pH, conductivity, and viscosity) [5,13,20,71,72].

Figure 5d demonstrates the change in growth rate and total charge as a function of anodization time and inset graph illustrates the variation of length with time: first 3 h, the length increases linearly and then the rate of increase reduces, e.g., the tube length for 4 h anodization is ~ 1.2 μm and for 24 h is ~ 1.6 μm . It is known that the charge consumption is a significant parameter that determines the growth rate of NTs (in an electrolyte with high pH). However, we observed that in an electrolyte with low pH, charge consumption increases while the growth rate decreases because of the etching effect (see Figure 5d). All these findings suggest that there is no direct relation between the length of tubular oxide layer and the consumed charge due to different etching efficiencies. Based on the findings, i.e. wall thickness, outer diameter of small nanotubes and top spacing reach a saturation for 4 h anodization for the studied anodization times of up to 24 h; hence an anodization time of 4 h is chosen for further investigations.

3.5 Influence of electrolyte composition

Figure 6 and 7 illustrate the effect of H_2O and HF content on the morphology of spaced nanotubes.

An overview of the morphological features of nanotubes fabricated in DEG electrolyte containing different amounts of water from 6 wt% (water comes from the 40 wt% HF and 0 wt% H_2O added) up to 26 wt% H_2O are given in Figure 6a and b. Evidently, the addition of water to the electrolyte changes the morphology (e.g., outer-inner diameter, tube-to-tube spacing and the length of NTs), namely, the outer diameter of the nanotubes increases from 147 ± 11 nm for 6 wt % H_2O to 185 ± 19 nm for 26 wt % H_2O . The most noticeable influence of water is however on the spacing as the top spacing reduces linearly from 134 ± 42 nm to 51 ± 11 nm (spacing at the top is due to the conical shape of nanotubes) and at the bottom, NTs become close-packed. I.e., at high water content small-diameter NTs and the two-size scale organization disappear, and close-packed arrays form. The water content decreases the spacing

not only due to the increase in diameter, but also due to a reduction in the inter-tube distance (the distance between the adjacent tube centers). This results in a higher nanotube density (the number of NTs per cm^2), see Figure 6b. Accordingly, Berger et al. [73] proposed that the increase in water content decreases the inter-pore distance, which is correlated with the tube outer diameter. It may be noted that another model by Overmeere et al. [74] suggests that electrostatic effects are the main driving force for pore initiation and the occurrence of inter-pore spacing.

Figure 7 illustrates the effect of HF content in the electrolyte on the resulting tube morphology. While in HF free electrolyte (only NH_4F is added) close-packed tube arrays with ripples along the tube sidewalls are formed, which show a broad size distribution of tubes, spaced tubular layers become apparent with the addition of HF. For close-packed arrays formed in HF free electrolyte, it is hard to distinguish the two-size scale organization from top SEM images (Figure 7a1). However, two different tube sizes are observable from the bottom view and the imprints of NTs on the Ti foil (see Figure 7a2 and the inset). Hence, in HF free electrolytes, small-diameter NTs can grow to the same length as big-diameter NTs. Whereas with HF addition, the size of small NTs decreases (e.g., the high HF content etches the small NTs) and the spacing drastically increases, inducing a transition from a close-packed to a spaced arrangement. While the dimples of small- and big-diameter NTs are visible in the case of HF free electrolyte (see inset in Figure 7a2), only the imprints of big-diameter NTs are visible for the HF containing electrolyte (see inset in Figure 7b2).

Figure 7c summarizes the variation of the inter-tube distance and tube density with HF concentration in the electrolyte; the inter-tube spacing is lowest for 0 wt% HF due to its morphology that shows similarities with the close-packed tubular arrays. The standard deviation of inter-tube distance is higher for the tubular layer obtained in 0 wt% HF content electrolyte, which is ascribed to the overgrown small-tubes in between big-tubes. Note that we have considered only the geometrical features of big-diameter NTs (e.g., inter-tube distance between big-tubes). The addition of more HF does not influence the tube nucleation sites, but promotes the chemical etching of NTs (especially of the small-diameter tubes). The experimental findings suggest that the growth of small NTs even larger obeys the electrolyte composition.

We also investigated the conductivity and pH of the electrolyte for different HF and H_2O content. While the pH of the electrolyte decreases from neutral pH (e.g., 7) in the case of no HF, to ~ 4 with 4 wt% HF addition, the conductivity slightly increases (from i.e., $\sim 311 \mu\text{S}/\text{cm}$ to $\sim 473 \mu\text{S}/\text{cm}$). The influence of H_2O addition on conductivity is more pronounced than that

of HF addition; for instance, the conductivity increases from $\sim 602 \mu\text{S}/\text{cm}$ (6 wt % H_2O) to $\sim 1901 \mu\text{S}/\text{cm}$ (24 wt% H_2O) and the pH is only slightly changed, i.e., decreases from ~ 4 to ~ 3.6 . However, we have not observed any decisive role of pH or electrolyte conductivity on space initiation between NTs within the parameter variation of the present work.

3.6 Mechanistic model for spaced tube formation

From above parameter investigations, it is evident that pore initiation followed by a spaced tube development is influenced by different aspects. Figure 8 shows top view SEM image of the oxide layer in the initial stage. For instance, in the very early stage of spaced tube formation, nanoscopic pores uniformly spread across the substrate (at moderate temperature and voltage, 120 s), as shown in Figure 8a. When we increased the electrode temperature and extended the anodization time to 300 s, the formation of large deep vortex-like pores become apparent (see Figure 8b). This can be attributed to the vortex movement (convection) of the electrolyte that occurs from the oxide-metal interface through the bulk electrolyte, leading to the pattern formation. Note that anodization at moderate conditions, e.g., 30°C and 30 V, leads to the formation of deep nanopores/breakdown sites but not to the vortex-like pattern formation. With time, in the area where deep breakdown sites or vortex-like pattern formed, nanotubes initiate. However, the findings indicate that heating the electrode fastens the self-organization process and improves the uniformity but it is not a decisive parameter for self-organized spaced tube formation, as spaced tubes grow also without any (external) heating effect or applied temperature.

Figure 9 shows the real SEM image and schematic model for spaced tubular structure in the early and the later stages of growth. The early stage of the hemispherical-like distinct oxide structures obtained in DEG and DMSO electrolyte, and the organization on two-size scales are shown in Figure 9a and b (inset shows the single hemispherical geometry). Obviously, different from the close-packed arrangement (where the hemispherical-like oxide structures are close-packed as well as continuous (crack-free like) from the very beginning [20,35,46]), the hemispherical-like (initial) oxide structures are spaced/separated, and with time secondary smaller features initiate in the space between bigger hemispherical-like oxide structures, as schematically illustrated in Figure 9c.

In the early stage (in 300 s, Figure 1c), initiation sites have uniform size and they are connected to each other except minor spacing in between neighboring sites. With time bigger hemispherical-like initiation sites are surrounded by smaller ones (in 480 s, Figure 1c). This phenomenon can be explained by two possible phenomena: *i*) blockage of the expansion and

the growth of nanotube by the neighboring NTs as a consequence of unequal field distribution/share. As a result, oxide initiates with smaller feature size, i.e, thinned down barrier layer and adjustment to the low field conditions, due to the limited access to current. *ii)* The formation of distinct initiation sites or space initiation can be also attributed to stress development (morphological instabilities) during pore initiation or breakdown that leads to the formation of distinct initiation sites (crack-like) in the oxide, in line with literature [26,38,57,75–78]. We believe that this will be followed by a healing effect or oxide growth (re-oxidation/re-passivation) with smaller feature size (non-uniform film growth or abnormalities in the oxide) in the non-passive gap/space area. I.e., first the large gap/space between the distorted hemispheres appear and then small hemispherical geometries (later evolve into sponge oxide) initiate in the gap area. Therefore, oxides with smaller feature size formed in the gap, might grow under complex etching/dissolution processes due to the quality of the oxide.

Similarly, Gösele et al. [57] reported that anodization of titanium at high voltage (near breakdown) induce compressive stress and consequently breakdown of the oxide layer. According to the report, the areas where electrical breakdown of the oxide occurs are immediately re-passivated and covered with TiO₂ again. Interestingly, in the areas where re-passivation occurs small pores initiate inside the pores.

The hemispherical-like oxide structures evolve into tubular structure as illustrated in Figure 9d and corresponding schematic drawing is shown in Figure 9e. Regarding inward diffusion, F-ions have a higher migration speed than O²⁻; thus fluoride enriches in the oxide/metal interface and forms a fluoride-rich layer, as observed in XPS depth profiling (Figure 2 and 9).

While the bottom of big-diameter NTs is embedded deep in the Ti substrate, small-diameter NTs are embedded in the fluoride-rich layer indistinctly and have thinner morphology/barrier layer (inset in Figure 9d shows an ion milled cross-section). This thin morphology (barrier layer) of the small NTs forces the shutting down of the old pore and reinitiation of a new one. One may speculate that a gap forms under the old small-diameter tube (between the old small-diameter tube and Ti substrate) as illustrated in Figure 9e — this morphology serves as a site for the next tube splitting/branching/growth sequence. The size of the newly formed small pores in the gap does not exceed the neighboring small-diameter NTs.

Thermal and morphological instabilities can provide extensive possibilities for the spontaneous appearance of vertically aligned spatial structures [26,38,57,75–80]. Therefore, for self-organized pore formation in spaced tube growth, stabilization of instabilities with two distinct different wavelengths should be considered. However, these effects of spatial organization can explain only the very beginning of tube growth, and the development of NTs

can be described by high classic field anodic effects: *i)* field assisted oxide formation/dissolution, *ii)* stress formation, *iii)* field distribution at the tube bottom, and *iv)* field assisted viscous flow of the barrier oxide film to the pore walls as described in the earlier works [26,56,57,65,76,81–87].

4. Conclusions

In the present work, we investigate the formation of vertically aligned spaced TiO_2 nanotubes. We show that the establishment of tube-to-tube spacing occurs in the early stage of tube growth. The growth sequence consists of nanoscopic pore initiation (some 10 s), the formation of spaced hemispherical-like oxide structure (after minutes), and the stable growth of nanotubes. According to the findings, the space/gap between large hemispherical-like features (oxide initiation sites) is occupied by smaller hemispherical-like geometries. With time large hemispherical-like structures develop into big-diameter nanotubes, while the small geometries grow into the sponge oxide or small-diameter nanotubes. In this two-size scale morphology, the diameter of small-tube and big-tube increases linearly with the applied potential, but the growth factor of small-diameter NTs is three times lower than that of big-diameter NTs. The experimental results suggest that the pore bottom/barrier layer of small-diameter NTs thins down sufficiently to allow a continued growth (e.g., the rapid repetition of growth and branching) under lower-field conditions.

The tube-to-tube spacing shows a strong dependence on anodization parameters (i.e., voltage, water content, and temperature). For instance, anodization at low voltage induces only porous/close-packed arrays, while at higher voltages (e.g., at ≥ 10 V) the oxide morphology changes from porous to spaced tubular layers; meanwhile, the spacing increases linearly with the applied voltage in the spaced tube region (voltage ≤ 40 V). In parallel, the sponge oxide amount increases, and establishes the tube-to-tube spacing, at even higher voltages (e.g., > 42 V) only sponge oxide forms. On the other hand, the water content and the temperature have an inverse relation with the spacing, since the sponge oxide content declines with increasing water content in the organic electrolyte or with increasing temperature. I.e., while a moderate anodization temperature improves the uniformity and leads to two-size scale organization, high temperatures yield a clean tubular morphology due to etching of small-diameter tubes/sponge oxide by the electrolyte.

From a mechanistic point of view, we believe that morphological instabilities and unequal field distribution induce the formation of initiation sites in regular intervals and two-size scale organization, consequently spaced nanotubes. The suggested mechanistic model is mainly

based on deductions from empirical observations of morphology, and surface analytical and electrochemical characterization results. A fully quantitative understanding of the mechanism of spaced NTs requires further experimental and parallel theoretical work.

Overall, the findings suggest that tube spacing is established by small-diameter nanotubes as we observed a direct correlation between the sponge oxide (consist in fact of small-diameter nanotubes) and tube-to-tube spacing. Usage of spaced NTs with controlled spacing is promising to fabricate interdigitated electrodes for electrochemical and photoelectrochemical (solar harvesting) energy conversion/storage applications, e.g., ion-intercalation devices, supercapacitors, photocatalyst, and solar cells.

Acknowledgements

The authors acknowledge the ERC, the DFG, the DFG “Engineering of Advanced Materials” cluster of excellence and DFG “funCOS” for financial support.

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Figure captions

Figure 1 a) 3-D drawings show the growth stages of spaced NTs from 30 to 900 s. b) Current density versus time profile for spaced tube formation for 4 h showing different growth stages (inset shows the current density-time plot for the first 480 s). c) Top SEM images of anodic oxide formed for 30 to 1800 s anodization (inset shows top or cross-section SEM images). (Anodizations were performed in DEG + 4 wt% HF + 0.3 wt% NH_4F + 7 wt% H_2O electrolyte at 30 V, 30 °C.)

Figure 2 The XPS depth profiling (and inset cross-section or top SEM image) of the oxide formed for **a)** 120 s, **b)** 300 s, **c)** 1800 s and **d)** 14400 s (only top ~200 nm of 1.2 μm). (Anodizations were done in DEG + 4 wt% HF + 0.3 wt% NH₄F + 7 wt% H₂O electrolyte at 30 V, 30 °C.)

Figure 3 a) Top and b) side view of tubes showing the big-diameter NTs embedded in small-diameter tube stacks fabricated at an applied voltage of 30 V. c) The change of diameter of big and small NTs with applied potential in the voltage range of 10-45 V. d) The growth factor versus time plot of small- and big-diameter NTs with applied potential in the voltage range of 10-45 V. e) Top SEM image of large diameter NTs with rich sponge oxide layer (inset shows the single large diameter NTs with branching in the lower part) grown at 42 V. f) SEM image shows the dimples of tubes and sponge oxide produced at 42 V. Side view of g) big- and h) small-diameter NTs indicate the barrier layer thickness formed at 42 V. (Anodizations were carried out in DEG + 4 wt% HF + 0.3 wt% NH_4F + 7 wt% H_2O electrolyte for 4 h at 30 °C.)

Figure 4 Top view (inset shows high magnification top and cross-section images) obtained **a)** without temperature control and **b)** with temperature control, at 30 °C. **c)** The current density-time profiles for NTs obtained without and with (at 30 °C) temperature control. Side view of tubes and sponge oxide stack obtained at **d)** 10 °C, and **e)** 30 °C. **f)** The side view of sponge oxide free tubular layer (inset shows top view of small- and big-diameter NTs) produced at 60 °C. **g)** The current density-time plot for NTs obtained between 10 to 60 °C. **h)** The variation of geometrical features with an electrode temperature in the range of 10 to 60 °C. **i)** The inter-tube distance and tube density change with electrode temperature in the range of 20 to 60 °C. (Nanotubes were fabricated in DEG + 4 wt% HF + 0.3 wt% NH_4F + 7 wt% H_2O electrolyte at 30 V for 4 h.)

Figure 5 Top view and inset side view of spaced NTs obtained for **a)** 30 min, **b)** 24 h anodization. **c)** Geometrical features (diameter, top spacing, wall thickness and the outer diameter of small nanotubes) variations as a function of time. **d)** Growth rate and total charge variation with time (inset shows length versus anodization time profile). (Anodizations were performed in DEG + 4 wt% HF + 0.3 wt% NH_4F + 7 wt% H_2O electrolyte at 30 V, 30 °C.)

Figure 6 a) Variation of geometrical features and length with water content in the DEG electrolyte. **b)** Inter-tube distance and tube density change with water content in the electrolyte. (Anodizations were performed in DEG + 4 wt% HF + H_2O content varied from 6 to 26 wt% H_2O + 0.3 wt% NH_4F electrolyte for 4 h at 30 V, 30 °C.)

Figure 7 **a1)** Cross-section (inset top view) of NTs and **a2)** bottom view (inset imprints) of tubular layer was produced in HF free (0 wt% HF) electrolyte. **b1)** Cross-section (inset top view) and **b2)** bottom view (inset imprints) of tubular layer was produced in 3 wt% HF containing electrolyte. **c)** Inter-tube distance and tube density change with HF content in the electrolyte. (Anodizations were done in DEG + HF content varied from 0 to 4 wt% HF + 0.3 wt% NH_4F + 7 wt% H_2O electrolyte for 4 h at 30 V, 30 $^\circ\text{C}$.)

Figure 8 **a)** The nanoscopic pores formed in the very early stage (first 120 s) of spaced tube growth in DEG electrolyte at 30 V, 30 °C. **b)** Vortex-like cells in the early stage of tube growth for 5 min at 60 V, 60 °C. (Anodizations were performed in DEG + 4 wt% HF + 0.3 wt% NH₄F + 7 wt% H₂O electrolyte.)

Figure 9 Real SEM images of an initiation of hemispherical tube bottom and two-scale organization in the early stage of growth produced after 480 s of anodization in **a)** DEG (inset shows high magnification image of single hemispheres, anodization was conducted in DEG + 4 wt% HF + 0.3 wt% NH₄F + 7 wt% H₂O electrolyte at 30 °C, 30 V), and **b)** DMSO electrolyte. (Anodization was performed in DMSO + 4 wt% HF + 0.3 wt% NH₄F + 7 wt% H₂O electrolyte at 30 V). **c)** 2D drawing of hemispherical (strong and weak) pore initiation in the early stage. **d)** Side view of DEG spaced NTs organized on two-size scale (inset shows the ion-milled side view of spaced tubular layer close to tube bottom indicates small- and big-tube). **e)** 2D illustration of small- (sponge oxide stacks) and big-diameter tube growth, and two-size scale organization.