

Ideally Hexagonally Ordered TiO₂ Nanotube Arrays

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Ideally hexagonally ordered TiO₂ nanotube layers were produced through the optimized anodization of Ti substrates. The Ti substrates were firstly covered with a TiN protecting layer prepared through atomic layer deposition (ALD). Pre-texturing of the TiN-protected Ti substrate on an area of $20 \times 20 \ \mu\text{m}^2$ was carried out by focused ion beam (FIB) milling, yielding uniform nanoholes with a hexagonal arrangement throughout the TiN layer with three different interpore distances. The subsequent anodic nanotube growth using ethylene-glycol-based electrolyte followed the pre-textured nanoholes, resulting in perfectly ordered nanotube layers (resembling honeycomb porous anodic alumina) without any point defects and with a thickness of approximately 2 μ m over the whole area of the pattern.

Since their introduction,^[1,2] self-organized TiO₂ nanotube layers have gained wide interest due to their potential application in a variety of different fields.^[3,4] As known from its sister material, porous anodic alumina, the control of the ordering of the nanotubes is essential for many applications, such as waveguides and photonic crystals.^[5,6] Over the past 10 years, many attempts have been made to improve the ordering of self-organized TiO₂ nanotube arrays and obtain similarly ordered structures as for porous alumina.^[7-11] However, this is a very challenging task. A simple way to increase the ordering of the nanotube layers is, to a certain extent, a two-step or three-step anodization of the Ti substrates.^[12-14] Other methods include mechanical, chemical, or electro-polishing of the Ti substrates before the anodization to reduce the surface roughness $^{\left[15-17\right] }$ or the use of high-purity Ti substrates.^[12,18] However, owing to the grain microstructure of Ti, the nanotube layers are usually just locally ordered, limited by the grain boundaries.^[18, 19]

Therefore, pre-texturing of the Ti substrate surface with nanoimprints before anodization, as is also known for porous

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alumina,^[5-7] was used to receive ideally ordered nanotube or nanopore arrays. Already in 2004, Choi et al.^[20] anodized nanoimprinted Ti. They used a 1×1 cm² master stamp consisting of Si₃N₄ pyramids (hexagonally arranged with a distance of 500 nm to the nearest neighboring pyramid) that they imprinted onto the Ti surface. By subsequent anodization in ethanolic HF solution, the highly ordered nanopore arrays with a pore depth of about 60 nm were received. Recently, similar attempts were carried out by Kondo et al.,^[21,22] who pre-textured the surface of a Ti foil or a Ti foil coated with a thin Al layer, respectively, by pressing a Ni mold with ordered convexes onto the surface. As a result, highly ordered nanoporous TiO₂ layers were received with thicknesses below 1 µm.^[21] However, owing to the hardness of Ti, the Ni mold could not be used repetitively in the study reported in Ref. [21]. Therefore, the same authors sputtered the Ti substrates with a thin Al layer and used the Ni mold repetitively to imprint the Al layer.^[22]

Another approach to directly pre-texture the Ti substrate before anodization is the use of focused ion beam (FIB) milling. Such patterning of the Ti surface was carried out by Chen et al.^[23-25] By using FIB-guided patterns, they received TiO₂ nanotube arrays with different shapes, such as squares, graphite lattices, or a sunflower arrangement of the nanotube arrays. However, in all cases, very short anodization times of 5-15 min were applied, in which the anodic nanotube arrays followed the given pattern. Therefore, just relatively thin nanotube layers of thickness from 900 nm to 1.3 µm were achieved. Furthermore, it can be hypothesized that, for longer anodization times, the nanotubes stop following the given pattern. This can be observed for the anodization of the sunflower pattern^[24] where, already after 5 min, the nanotube bottoms are not as perfectly ordered, as seen from the top views. Recently, Vega et al.^[26] received long-range-ordered nanotubular TiO₂ structures by using laser interference lithography to pre-texture the Ti foils before anodization. However, for this method, three different resists and four different etching steps were employed for the fabrication of the pattern, making the method rather complicated. Furthermore, nanotube layers thinner than 1 µm were achieved. Even though these most recent papers^[21-26] represent a significant advancement in the state-of-the-art in terms of TiO₂ nanotube ordering, all published scanning electron microscopy (SEM) images clearly display a number of point defects within the nanotube ordering (voids, heptagons, pentagons, etc.). In addition, all published patterns in these papers were smaller than $10 \times 10 \ \mu m^2$.

In this Communication, for the first time, the surface of polished Ti sheets was protected by a thin TiN layer and pre-textured with hexagonally arranged nanoholes by using FIB, with the goal of obtaining perfectly ordered and point-defect-free





 TiO_2 nanotube layers over the whole pattern (20 \times 20 μm^2) upon subsequent anodization.

Within preliminary experiments, several different polymeric resists and inorganic films were explored. However, with the exception of a thin TiN layer produced by atomic layer deposition (ALD), none of them remained attached to the Ti substrate for longer than few minutes, owing to the harsh conditions during anodization (fluoride etching, oxygen bubble formation, high current flows, etc). Therefore, a thin TiN layer produced by ALD was used as a resist to protect the surface of the Ti substrate.

Figure 1 a shows the pattern and Figure 1 b the nanoholes fabricated in the Ti substrates through the protecting TiN layer, using FIB for an interpore distance of S = 180 nm. These nanoholes acted as initiation sites for the nanotube growth during anodization and were approximately 55 nm deep. Owing to the TiN thickness of around 10 nm, the nanoholes were fabricated into the Ti substrate to the depth of about 45 nm. However, the reason for the TiN layer was to protect the rest of the Ti substrate from anodization and, thus, to allow longer anodization times resulting in ideally ordered TiO₂ nanotube layers of the highest aspect ratio possible. Figure 1 c shows the AFM and profilometry images of the fabricated nanoholes. It is clear that the nanoholes have a similar depth of approximately 55 nm.



Figure 1. a) Scheme of the hexagonally arranged pattern of nanoholes fabricated through the TiN layer on the Ti substrates, b) SEM image of the pattern before anodization with an interpore distance of 180 nm, c) AFM and profilometry image showing the depth of the fabricated nanoholes, d) SEM image of the anodized pattern $(20 \times 20 \ \mu\text{m}^2)$ in an electrolyte containing 44 mm NH₄F, and e) an enlargement of (d), showing the border between the anodized pattern and the area that is not pre-textured. *S*: interpore distance (120 nm, 150 nm and 180 nm); *d*: diameter of the nanoholes (ca. 50 nm).

Figure 1d shows the whole area of the pattern with S = 180 nm after anodization. As can be seen, after anodization at 60 V for 30 min, the pattern was still maintained over the whole area. This means the nanotubes followed the given pattern. Figure 1e shows the intersection between the pattern and the area of the substrate that was not pre-textured. It is clearly visible that the nanotubes followed the pattern, whereas only very few and randomly ordered pores were grown on the rest of the substrate. This suggests that during the anodization time (30 min) the TiN protection layer was not completely stable and attacked by the fluoride ions present in the electrolyte. Therefore, nanotubes started to grow randomly on this part as well. However, the strongly preferential growth of the TiO₂ nanotubes occurred through the fabricated nanoholes.

On each TiN-protected Ti substrate, three nanohole patterns were fabricated with S = 120, 150, and 180 nm. Within preliminary experiments, TiO₂ nanotube layers were produced under the same conditions in the electrolyte containing 88 mm on the Ti substrates without a pattern. Subsequent statistical evaluation revealed that the mean *S* value between the nanotubes was 150 nm. The aim with the pattern shown in Figure 1 was, therefore, to prepare one pattern with this natural spacing (for the given anodization conditions) and two other with a smaller *S* value (i.e. 120 nm) and a larger *S* value (i.e. 180 nm).

Figure 2 displays the three different patterns on substrates anodized in electrolytes with different NH₄F concentrations. Clearly, in the 44 mM NH₄F electrolyte, the nanotubes followed all three given patterns. In the case of the 88 mM NH₄F electrolyte, the nanotubes followed the patterns with S = 120 and 150 nm. For S = 180 nm, additional nanotubes were formed in between the nanoholes, as the distance was too large and the etching rate in the more concentrated electrolyte was too high. The fact that no additional nanotubes were formed for this *S* value in the 44 mM NH₄F electrolyte can be attributed to the lower fluoride ion content in combination with an anodization time of just 30 min, which was too short for the formation of additional nanotubes through the protecting TiN layer.



Figure 2. Top views of the anodized patterns in different electrolytes at 60 V for 30 min. All scale bars show 200 nm. S: interpore distance.





For the electrolyte with 176 mM NH₄F, the nanotubes did not follow any of the given patterns perfectly. Even though the protecting TiN layer was still present on the surface after anodization, including the patterns, the TiO₂ nanotubes formed under this layer were naturally organized and not perfectly ordered. This can be connected to the faster etching rate and nanotube growth in the more concentrated fluorideion-containing electrolyte. However, the greatest concordance between the pattern and the TiO₂ nanotube growth was found for S = 150 nm. This was in agreement with the initial calculation of the mean *S* value.

These results show clearly that a strong protection layer on the Ti surface is necessary for the nanotubes to follow exactly the given pattern for anodization times longer than just a few minutes. Furthermore, the TiN acts as a certain planar support, preventing disintegration of the nanotubes within the layer, holding nanotubes tight and stimulating the growth exactly as it is needed—hexagonally packed.

Figure 3 shows SEM images of TiO_2 nanotubes obtained for the three different patterns in the electrolyte containing 44 mM NH₄F. This figure shows that the TiO_2 nanotubes grew in a hexagonal shape under the TiN protecting layer and kept their shape as well as their ordering across the whole nanotube length, as the hexagonal shape was observed at the top of the nanotubes as well as from the dimples left in the Ti substrate after removal of the nanotube layers. Furthermore, the protecting layer was still present after the anodization and not attacked by the electrolyte. This means that, on the pre-textured parts of the substrate, TiO_2 nanotubes were only grown



Figure 3. SEM images of TiO₂ nanotubes obtained on different patterns in an electrolyte containing 44 mm NH₄F: a) top view, S = 150 nm; b) single nanotubes, S = 150 nm; c) cross-section, S = 180 nm; d–f) dimples, S = 180 nm. The dotted lines in (f) should help to see the arrangement of the dimples.

on the given initiation site. Moreover, it is clear that, exactly one TiO_2 nanotube was grown from each nanohole. Thus, perfectly hexagonally ordered TiO_2 nanotube layers were obtained, resembling a honeycomb porous anodic alumina with ideal hexagonal ordering.^[5] Figures 3 d–f show the dimples of the nanotubes in the Ti substrates after removal of the nanotubes. It is clear that the nanotubes are ideally hexagonally arranged in the shown area of approximately $2.2 \times 1.7 \ \mu\text{m}^2$ (Figure 3 e) without any defects, such as heptagons or pentagons.

The cross section shown in Figure 3c depicts a TiO₂ nanotube layer thickness of approximately 2 μ m. Compared to the literature,^[21-24,26] these are the thickest and, at the same time, ideally hexagonally ordered TiO₂ nanotube layers obtained to date.

In conclusion, the formation of ideally hexagonally ordered TiO₂ nanotube layers was achieved by protecting the surface of a Ti substrate with a TiN layer and pre-texturing this layer by FIB milling, yielding pattern of hexagonally arranged nanoholes. The nanoholes acted as initiation sites for the nanotube growth. Therefore, the TiO₂ nanotubes followed the given patterns perfectly when a mild electrolyte, that is, with a low NH₄F content (44 mm), was employed. Owing to a reasonably long anodization time, approximately 2 µm thick ideally ordered TiO₂ nanotube layers were obtained over the whole pattern area of $20 \times 20 \,\mu\text{m}^2$, which is the largest area reported. The presented results clearly show that ideal ordering of TiO₂ nanotube layers is feasible, resulting in a structure similar to honeycomb porous alumina. The present approach may pave the way for further exploitation of these layers in various applications and for other valve metal oxide nanoporous and nanotubular structures to be prepared with the same or similar ordering degree.

Experimental Section

The Ti sheets (Goodfellow, 2 mm thick sheets, 99.6+% purity, prepolished) were mechanically lapped by using diamond suspensions (first 6 μ m particles, afterwards 1 μ m particles) and polished with OPS suspensions to obtain a mirror-like surface with a mean roughness of approximately 3 nm. The polished substrates were degreased by sonication in isopropanol and acetone, before being rinsed with isopropanol and dried in air.

The surface of the polished Ti sheets was coated with a TiN layer of a nominal thickness of 9.8 nm by using an ALD tool (thermal ALD, TFS 200, Beneq). Titanium tetrachloride (TiCl₄, Strem, 99.9999%) and ammonia (NH₃, Messer, 99.999%) were used as titanium and nitrogen precursors, respectively. ALD processes were carried out at a temperature of 350 °C, and using N₂ (99.9999%) as the carrier gas at a flow rate of 400 standard cubic centimeters per minute (sccm). Under these deposition conditions, one ALD growth cycle was defined by the following sequence: TiCl₄ pulse (300 ms)–N₂ purge (4 s)–NH₃ pulse (5 s)–N₂ purge (8 s). The nominal thickness of the TiN layer was estimated from the growth per cycle value of the process at 350 °C (ca. 0.29 Å/cycle). Thus, the ALD process of 338 cycles results in a nominal thickness of 9.8 nm.

The fabrication of nanohole arrays was carried out by FIB (LYRA3 FIB-SEM, Tescan). The kinetic energy of gallium ions was 30 keV and ion beam current was set at approximately 1 pA. Three differ-

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ent hexagonal patterns were milled through the TiN layer into the surface of the Ti sheets with a nanohole diameter of 50 nm, a nanohole depth of about 55 nm (measured by atomic force microscopy, AFM, Dimension Icon, Bruker), and interpore distances of 120, 150, and 180 nm. All patterns had an area of $20 \times 20 \ \mu m^2$.

The anodization of the substrates were carried out in ethylene glycol based electrolytes containing 1.5 vol% deionized water and NH₄F of different concentrations, that is, 44, 88, or 176 mm. All electrolytes were prepared from reagent-grade chemicals. Before the first use, the electrolytes were aged for 9 h through anodization of blank Ti substrates at 60 V to obtain electrolytes with the best performance.^[27] The electrochemical setup consisted of a twoelectrode configuration, using a platinum foil as the counter electrode, and the Ti sheets (working electrodes) were pressed against an O-ring of the electrochemical cell, leaving 1 cm² open to the electrolyte. Electrochemical experiments were carried out at room temperature by employing a high-voltage potentiostat (PGU-200 V, IPS Elektroniklabor GmbH). The anodizations were carried out at 60 V for 30 min after sweeping the potential from 0 to 60 V with a sweeping rate of 1 Vs⁻¹. After anodization, the Ti sheets were rinsed and sonicated in isopropanol and dried.

The structure and morphology of the TiO₂ nanotube layers were characterized by SEM (JEOL JSM 7500F).

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Conflict of Interest

The authors declare no conflict of interest.

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