

SELF-ORGANIZED TiO₂ NANOTUBE ARRAYS AND THE MECHANISM OF TUBE GROWTH

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Abstract

TiO₂ nanotubes are highly promising for application in various fields. Many publications are concerned with nanotubes prepared by the anodization of titanium foil. This work presents TiO₂ nanotube arrays fabricated by the anodic oxidation of thin titanium layer. Titanium layer is sputter-deposited on silicon wafer with thermal SiO₂ layer. Nanotubes were prepared in organic electrolyte containing water and different amounts of ammonium fluoride. The influence of different amount of ammonium fluoride is observed by scanning electron microscopy (SEM). Removing initial oxide barrier layer plays a significant role in successful preparation of nanotubes. Under optimized conditions, i.e. a good balance between oxidation and etching during anodization, nanotube arrays with uniform configuration are obtained.

Keywords: Titanium dioxide, nanotubes, growth mechanism, anodic oxidation

1. INTRODUCTION

TiO₂ is one of the most studied material in various research and application fields. It is known to be nontoxic, environmentally friendly, corrosion-resistant material, frequently used in paint, white pigments or sun-blockers. The key functional properties are almost unique ionic and electronic behaviour of this oxide. TiO₂ is a wide-bandgap semiconductor ($E_g \approx 3$ eV) in all its crystal forms which make it suitable for its use in photovoltaic solar cells [1] and for photocatalytic reactions [2]. Photogenerated electron pairs (electrons and holes) can be used for water splitting or potentially for the treatment of drinking water from persistent organic pollutants [3,4]. Also this material is highly promising in applications in electrochromic devices [5], antifogging [6], self-cleaning [7], biomedical [8-10] and smart-surface coatings [8] or sensors [11].

The TiO₂ nanostructures could be fabricated by various methods such as sol-gel [3], hydrothermal, solvothermal [12] anodic oxidation [13] or using template [14]. Among these methods, electrochemical anodic oxidation (AO) has become one of the most popular because of its high controllability of fabrication parameters and especially ability to fabricate 1D TiO₂ nanostructures. High purity Ti foils are usually used and anodized in fluoride containing electrolytes. Shapes and dimensions (e.g. nanotube lengths of several hundreds of μm) can be varied by thicknesses of anodized foils and electrolyte compositions [14]. Despite the large number of publications on anodized titanium foil, there are only few studies devoted to the anodization of titanium thin films deposited on silicon or conductive glass substrates. However AO of thin films is challenging because of one key problem, i.e. to find a balance between oxidation of titanium and chemical dissolution of TiO₂ during AO. By changing the electrolyte composition and varying anodization voltage, different shapes of defect-free nanostructures can be obtained [5].

Main aim of this study is to fabricate TiO₂ nanotubes (NTs) using thin titanium film sputter-deposited on silicon wafer and to review the current state of art of the growth mechanism leading to the formation of anodized TiO₂ NTs in fluoride containing electrolyte.

2. MATERIALS AND METHODS

2.1. Materials

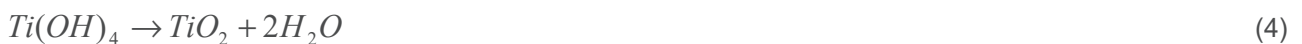
Titanium (99.99%, Porex, CZ), ethylene glycol (C₂H₆O₂, p.a., Penta, CZ) and ammonium fluoride (NH₄F, Reidel-de Haen, DE). Deionized water was obtained from Millipore RG system MilliQ (Millipore Corp., USA). All chemicals were used as purchased without any purification.

2.2. Preparation of TiO₂ NTs

A titanium film of 1 μm thickness was sputter-deposited onto silicon wafer with 1 μm of thermal SiO₂. Before AO, this substrate was consecutively immersed into acetone, isopropylalcohol, and deionized water to remove the impurities and then dried by compressed air. The AO was realized in the system with controlled circulation of electrolyte in two-electrode configuration and using power supply controlled by LabView program. The substrate operates as a working electrode and the gold tube was used as a counter electrode. The potential was kept constant during the whole AO and different values in the range of 10-60 V were tested. The changing current during AO was monitored. The electrolyte solution was prepared from ethylene glycol containing ammonium fluoride (0.3-1.4 wt%) and deionized water (2 vol%). The anodized titania was rinsed with deionized water and dried in air.

3. RESULTS AND DISCUSSION

During the preparation of titania nanostructured surfaces by direct AO of Ti thin layer, we identified three different phases (I.-III.) of the anodization process as can be seen in **Fig. 1**, which represents current vs time plot for anodization at 20 V. During the first few seconds, a high value of current is detected meaning the Ti started to be oxidized to Ti⁴⁺ ions at the surface while releasing electrons into electrolyte solution (Eq.1). The effect of electric field leads to the dissociation of water into OH⁻ and O²⁻ anions (**Fig. 2**). Both of these ions recombine with Ti⁴⁺ and create either titanium hydroxide (Eq.2) or TiO₂ (Eq.3) in simple single process. Titania is further produced when the titanium hydroxide releases water by condensation reaction (Eq.4).



After a complete creation of initial titanium oxide barrier layer, the current quickly drops to a local minimum (I.). In order to maintain the oxidation process, the ions (O²⁻, OH⁻, Ti⁴⁺ and F⁻) have to pass through the high resistance barrier layer. Fluoride anions attack the barrier oxide layer under the influence of the electric field generating the small dimples unregularly over the whole surface. This step results in formation of F⁻ rich layer at the metal-oxide interface. Thus the main role of fluorides is to maintain a thinner barrier layer by chemical etching of the oxide layer (Eq.5). In addition, they participate in complexation of Ti⁴⁺ species at the oxide-electrolyte interface (Eq.6). In the second stage (II.), the current slowly increases due to the creation of pores. Once the titanium layer is fully oxidized, the current drops steeply close to the 0 A and stays constant (III.).



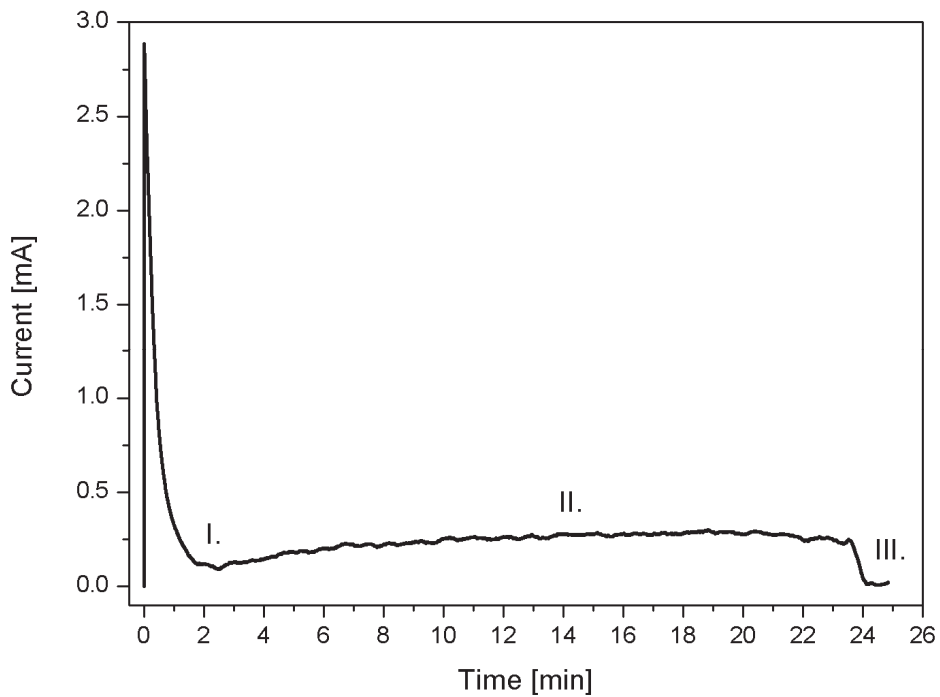


Fig. 1 Current vs time plot for AO of thin titanium layer. The I.-III. numbers highlight the different stages during AO

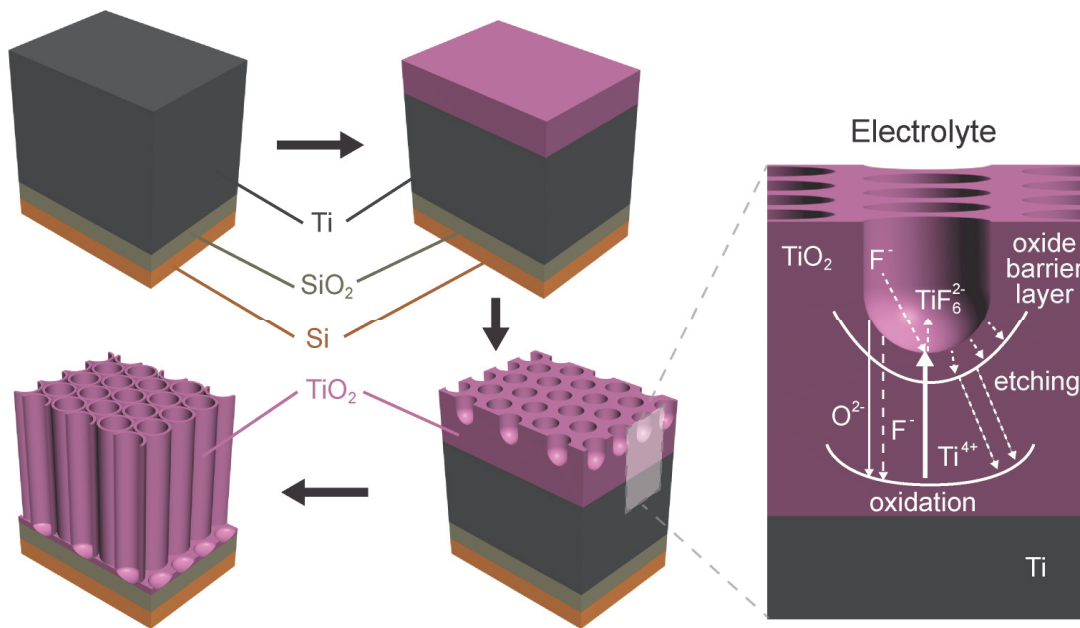


Fig. 2 Schematic illustration of TiO₂ NTs growth

The titania nanostructured surfaces were characterized by SEM - see **Fig. 3** which shows the topography of TiO₂ anodized at 20 V in ethylene glycol based electrolyte containing different amounts of ammonium fluoride and 2 vol% of water. The shape of nanostructures strongly depends on the balance between Ti oxidation and dissolution. Namely, the nanoporous structure is visible only in **Fig. 3A** because of lower concentration of fluoride ions in the electrolyte. In this case, electrochemical oxidation of Ti dominates in the process and titania NTs are blocked by the surface layer consisting of Ti(OH)₄ or TiO₂. Unblocked freestanding NTs were fabricated

in the electrolyte solution containing 1.2 wt% NH₄F (**Fig. 2B**). NTs in **Fig. 3C** are prepared in electrolyte containing more ammonium fluoride (1.4 wt%). These free standing nanotubes are clearly visible, but the fluoride content should be decreased, because the etching process was very intensive.

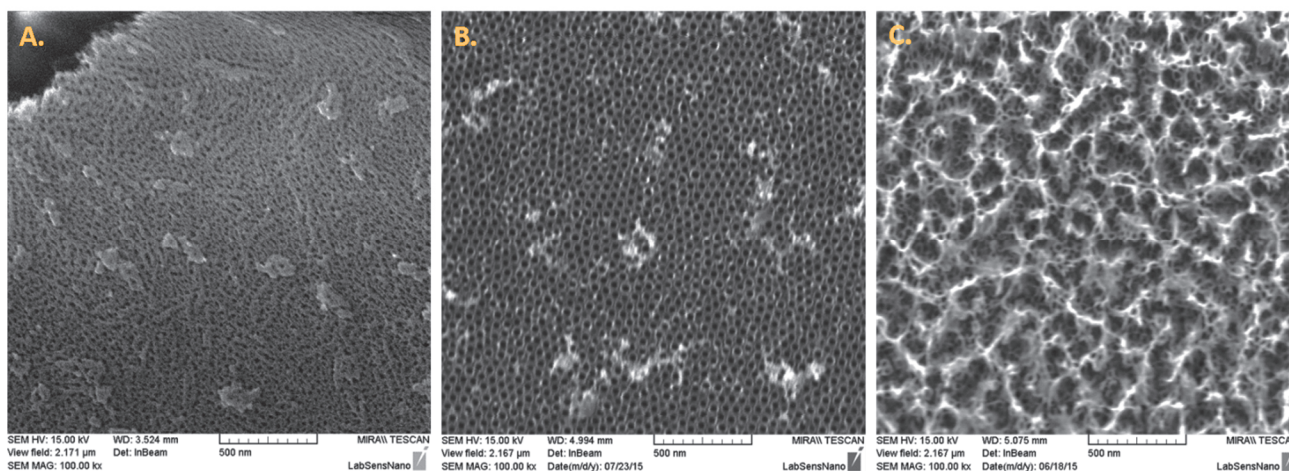


Fig. 3 TiO₂ surfaces created in electrolyte containing: A) 0.3 wt% NH₄F, B) 1.2 wt% NH₄F and C) 1.4% NH₄F

We observed that the achievement of nanotubes by oxidation of ultrathin titanium layer at higher voltage is very difficult due to the competition between etching and oxidation processes. When the anodization voltage is increased, the amount of fluoride ions has to be increased from the anodization beginning in order to fully etch the initial barrier layer and to form unblocked NTs.

4. CONCLUSION

The present work demonstrates a method for direct anodic transformation of Ti thin layer deposited on silicon wafer into nanotubular TiO₂ array. Simple AO in electrolyte containing ethylene glycol and NH₄F allows the controlled fabrication of ordered and highly regular TiO₂ NTs. The explanation of NTs growth mechanism, analysis of anodization curves, and SEM characterization of resulting nanostructures enables us to better understand how the NTs creation can be controlled. Fabricated TiO₂ NTs have very good potential for future sensing, biomedical or photocatalytic applications, mainly in advanced degradation of persistent organic pollutants in drinking water, etc.

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REFERENCES

- [1] FISCHER, K. et al. Nanoneedle and nanotubular titanium dioxide - PES mixed matrix membrane for photocatalysis. *Applied Catalysis B: Environmental*, 2014, vol. 160-161, no. 0, pp. 456-464. ISSN 0926-3373.
- [2] NAKATA, K. a FUJISHIMA, A. TiO₂ photocatalysis: Design and applications. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 2012, vol. 13, no. 3, pp. 169-189. ISSN 1389-5567.
- [3] PIHOSH, Y. et al. Ubiquitous element approach to plasmonic enhanced photocatalytic water splitting: the case of Ti@TiO₂ core-shell nanostructure. *Nanotechnology*, 2014, vol. 25, no. 31, pp. 8. ISSN 0957-4484.
- [4] RAY, A. K. a BEENACKERS, A. A. C. M. Development of a new photocatalytic reactor for water purification. *Catalysis Today*, 1998, vol. 40, no. 1, pp. 73-83. ISSN 0920-5861.

- [5] BERGER, S. et al. Transparent TiO₂ Nanotube Electrodes via Thin Layer Anodization: Fabrication and Use in Electrochromic Devices. *Langmuir*, 2009, vol. 25, no. 9, pp. 4841-4844. ISSN 0743-7463.
- [6] EMELINE, A. V. et al. Factors Affecting UV-Induced Superhydrophilic Conversion of a TiO₂ Surface. *The Journal of Physical Chemistry C*, 2013, vol. 117, no. 23, pp. 12086-12092. ISSN 1932-7447.
- [7] PATROCINIO, A. O. T. et al. Layer-by-Layer TiO₂/WO₃ Thin Films As Efficient Photocatalytic Self-Cleaning Surfaces. *Acs Applied Materials & Interfaces*, 2014, vol. 6, no. 19, pp. 16859-16866. ISSN 1944-8244.
- [8] ROY, P. et al. TiO₂ Nanotubes: Synthesis and Applications. *Angewandte Chemie International Edition*, 2011, vol. 50, no. 13, pp. 2904-2939. ISSN 1521-3773.
- [9] HUO, K. et al. Fabrication, modification, and biomedical applications of anodized TiO₂ nanotube arrays. *Rsc Advances*, 2014, vol. 4, no. 33, pp. 17300-17324.
- [10] DRBOHLAVOVA, J. et al. Effect of Nucleic Acid and Albumin on Luminescence Properties of Deposited TiO₂ Quantum Dots. *International Journal of Electrochemical Science*, 2012, vol. 7, no. 2, pp. 1424-1432. ISSN 1452-3981.
- [11] SOLOVEI, D. et al. Chemical Sensor Platform for Non-Invasive Monitoring of Activity and Dehydration. *Sensors*, 2015, vol. 15, no. 1, pp. 1479-1495. ISSN 1424-8220.
- [12] MOHAN, R. et al. Water-dispersible TiO₂ nanoparticles via a biphasic solvothermal reaction method. *Nanoscale Research Letters*, 2013, vol. 8, pp. 4. ISSN 1556-276X.
- [13] DRBOHLAVOVA, J. et al. Self-ordered TiO₂ quantum dot array prepared via anodic oxidation. *Nanoscale Research Letters*, 2012, vol. 7, pp. 4. ISSN 1931-7573.
- [14] WEICKERT, J. et al. Controlled Growth of TiO₂ Nanotubes on Conducting Glass. *Chemistry of Materials*, 2011, vol. 23, no. 2, pp. 155-162. ISSN 0897-4756.