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Self-organized Anodic TiO_2 Nanotube Layers: Influence of the Ti substrate on Nanotube Growth and Dimensions

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ABSTRACT

In this contribution, various Ti thin substrates were explored and compared for the anodic growth of self-organized TiO_2 nanotube layers for the first time. In order to evaluate differences in the electrochemical anodization characteristics and the tube dimensions, five different Ti substrates from four established suppliers were anodized in the widely used ethylene glycol electrolytes containing 88 mM NH_4F and 1,5 vol.% water. Two anodizations were carried out to elucidate an influence of the pre-anodized substrates used for the second anodization. By thorough evaluation of the nanotube dimensions, large variations between the dimensions of the nanotubes were found for the different substrates, ranging from ~32 μm to ~50 μm for the nanotube length and from ~109 nm to ~127 nm for the nanotube diameter after the second anodization. Upon AFM measurements, Goodfellow Ti substrates (99.99% purity), yielded the smoothest surface and the highest degree of ordering from all substrates. Moreover, considerably different consumption of Ti substrates via anodization was revealed by profilometric measurements between the original non-anodized part of the Ti substrates, and the anodized part after the removal of the nanotube layer. Orientation imaging microscopy revealed considerable differences in the size and orientation of the substrate grains.

1. Introduction

Since their introduction [1,2], TiO_2 nanotube layers produced by anodization of Ti have attracted wide interest due to their application in various fields, such as dye-sensitized solar cells [3–7], sensors [8–10] or photocatalysis [11–13]. Overviews about applications are also given in several review articles [14–16]. During the past 10 years, considerable attention was given on the control of the nanotube dimensions, i.e. length and diameter, and the ordering of the nanotubes. The nanotube diameter and length can be controlled by the applied potential, the anodization time and the electrolyte used for anodization [17–19]. Thus, the first generation of TiO_2 nanotubes produced in HF-containing electrolytes did not exceed a length of approximately 500–600 nm due to a fast dissolution of TiO_2 by HF [20]. Later on, other electrolytes, i.e. glycerol [21,22] and ethylene glycol [23] based electrolytes, containing NH_4F instead of HF were explored, which enabled researchers to produce a wide range of nanotube layers with different aspect ratios.

It is known from the sister material – porous alumina – that hexagonal packing and improved ordering of pores in general is crucial for numerous other applications, such as waveguides and photonic crystals [24,25]. Therefore, efforts have been carried out to improve the degree of ordering of TiO_2 nanotube arrays. The simplest way to produce ordered TiO_2 nanotubes turned out to be the repetitive anodization of the same substrate, after the removal of the nanotube layer grown during the first anodization, and applying a second anodization step [26–29]. Other attempts included either polishing of the Ti surface by various means (such as chemical, mechanical and/or electro- polishing) to reduce its roughness, [30,31], or pre-texturing of Ti by a nanoimprinting process [32]. However, the degree of ordering and the ordering range are very likely strongly influenced by the microstructure of Ti, which has numerous grain boundaries. Nevertheless, to the best of our knowledge no studies have yet been reported that compare different Ti substrates in terms of roughness, microstructure and

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electrochemical characteristics, and their influence on the nanotube characteristics.

Therefore, in this work, five different Ti substrates from established suppliers were investigated (and compared) with respect to the electrochemical characteristics of the nanotube growth, and their resulting dimensions. Two repetitive anodizations on each substrate were performed followed by a thorough check of all resulting layers by scanning electron microscope (SEM). Furthermore, the roughness of the Ti substrates after the second anodization was analysed by atomic force microscope (AFM). Additionally, the average depth of the anodized area was measured using a profilometer. Finally, the microstructure of the substrates was investigated by electron backscatter diffraction (EBSD) technique.

2. Experimental

Five types of Ti substrates of different purities commonly used for the TiO_2 nanotube growth by researchers worldwide were purchased from four established suppliers for comparison; Sigma-Aldrich (0.127 mm, 99.7% purity, marked as SiAl), Advent Materials (0.125 mm, 99.6+% purity, marked as AM), Chempur (0.125 mm, 99.6% purity, marked as CP), Goodfellow (0.125 mm, 99.6+% purity, marked as GoFe99.6+%) and Goodfellow (0.125 mm, 99.99% purity, marked as GoFe99.99%).

The Ti substrates were degreased prior to anodization by sonication in isopropanol and acetone, then rinsed with isopropanol and dried in air. The electrochemical setup consisted of a 2 electrode configuration using a platinum foil as the counter electrode, while the Ti substrates (working electrodes) were pressed against an O-ring of the electrochemical cell, leaving 1 cm^2 open to an electrolyte. Electrochemical experiments were carried out at room temperature employing a high-voltage potentiostat (PGU–200 V, IPS Elektroniklabor GmbH).

For the electrolyte, ethylene glycol was used containing 1.5 vol. % deionized water and 88 mM NH_4F. All electrolytes were prepared from reagent grade chemicals. Before use, all electrolytes were aged for 9 hours by anodization of blank Ti substrates at 60 V under the same conditions as for the main anodization experiments. If not stated otherwise, Ti substrates were anodized for 14 hours during the first anodization and for 6 hours during the second anodization. The first nanotube layer was removed by cathodic reduction of the substrate, as reported previously [33], followed by sonication of Ti in isopropanol, in preparation for the second anodization. For all experiments new electrolytes were employed, which were freshly aged and not used in any previous anodizations, resulting in electrolytes of the same age for all anodizations. At the beginning of the anodization process, the potential was swept from 0 V to 60 V with a sweeping rate of 1 V/s. After anodization, the Ti substrates were rinsed and sonicated in isopropanol and dried.

The structure and morphology of the TiO_2 nanotubes were characterized by a field-emission SEM (JEOL JSM 7500F). Dimensions of the nanotubes were measured and statistically evaluated using proprietary Nanomeasure software. For each condition used in this work, average values and standard deviations were calculated from at least 3 different locations on 2 samples of each condition, with a high number of measurements ($n \geq 100$).

An Atomic Force Microscope (AFM, Solver Pro M, NT-MDT) was used to evaluate the surface topography of the substrates in semi-

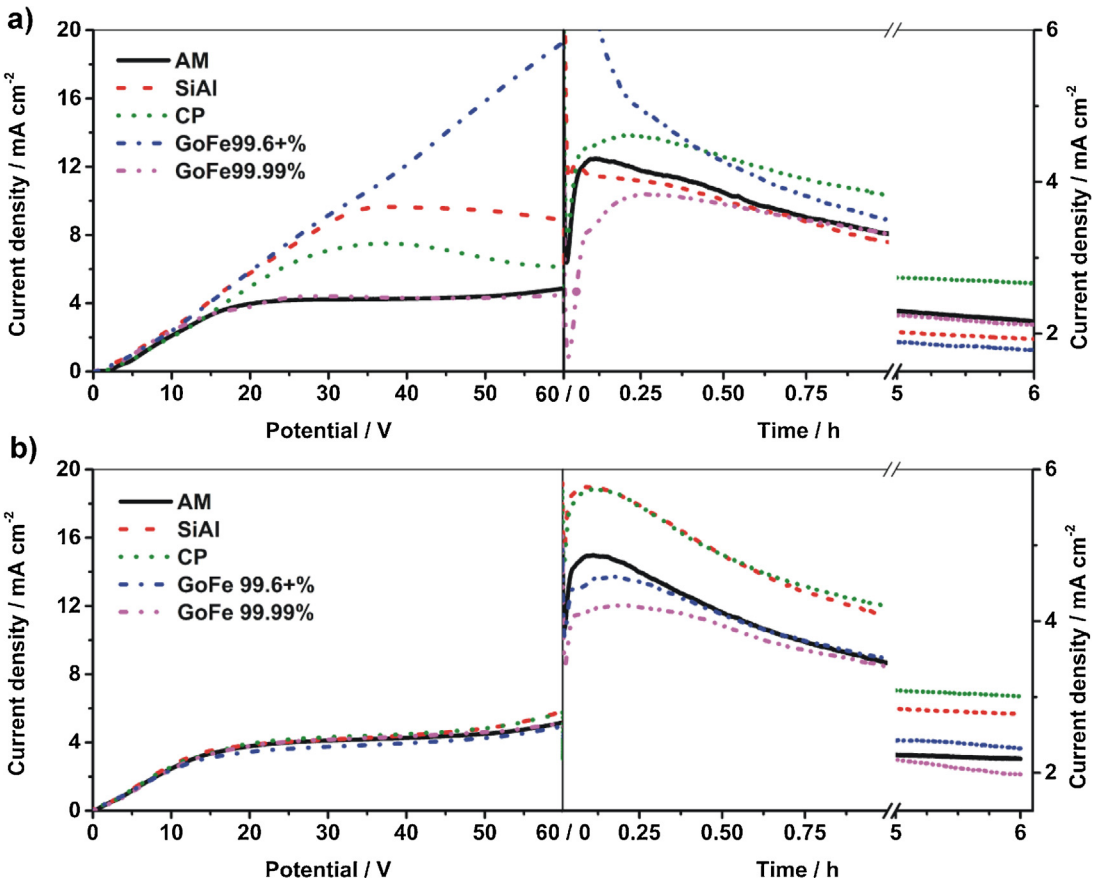

Fig. 1. Polarization plots (left) and current transients (right) recorded for the anodization of different Ti substrates for the 1st anodization (a) and for the 2nd anodization (b). The curve for the 1st anodization shows the initial 6 hours of the total time of 14 hours.