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From anodic TiO_2 nanotubes to hexagonally ordered TiO_2 nanocolumns

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ABSTRACT

We report on the formation of hexagonally ordered TiO_2 nanocolumnar layers by electrochemical oxidation in a fluoride containing electrolyte, using self-organizing nanotube formation conditions at elevated potentials and low temperatures. The influence of the substrate temperature on the nanocolumn morphology and composition is investigated and characterized by FE-SEM and EDX. The origin of these nanocolumns can be attributed to a thickening of the inner tube wall of the double wall structure of self-organized TiO_2 nanotubes. Furthermore, a transition from nanocolumnar to nanotubular structure can be established by changing the applied voltage or applying a post-immersion treatment.

1. Introduction

In 1999 Zwilling et al. reported a straightforward and simple approach to form self-organizing nanostructured oxide layers by electrochemical anodisation in diluted HF electrolytes [1]. Later on this approach was transferred to other valve metals (e.g. titanium, zirconium, hafnium, etc.) [2,3]. This process results in highly ordered arrays of closely packed vertically aligned tubes or pores. Over the past few years, considerable progress was made particularly to optimize nanotubular morphology of TiO_2 [4–6]. TiO_2 nanotube arrays have attracted most attention as the material provides a wide range of functional properties [7]. Nanotubes are highly interesting for biomedical applications [8,9] (as a biocompatible material or drug release systems), as the material is photo-corrosion resistant, and shows a high photo-catalytic activity [10,11]. Moreover, these structures proved to be very efficient using them for catalytic chemical reactions [12], sensing applications [13], or as catalyst-host in fuel cells [14].

In order to achieve enhanced control over the electronic and optical properties of TiO_2 nanotubes, various doping approaches with suitable elements, e.g. C [15,16] and N [17,18] or various transition metals [19–22] were reported. Particularly band-gap tailoring approaches, incorporating carbon upon a high temperature reduction treatment were able to produce semimetallic layers of TiO_2 and TiO_2 nanotubes with enhanced electronic [23] and mechanical properties [24]. For an overview on developments in research in this field of self-organized TiO_2 nanotubes some review articles [25,26] are available. Recent reports showed that by changing the electrochemical conditions different anodic nanostructures can be achieved. For example, replacing fluorides with chlorides as active species results in a rapid growth of so called RBA (rapid breakdown anodisation) nanotubes [27], whereas by alternating the applied voltage nanobamboo and nanolace structures [28] can be achieved. In the present work we report on the origin of nanocolumnar morphologies observed upon anodisation at controlled substrate temperatures using Peltier cooling.

2. Experimental

Titanium foils (Goodfellow, England) with a purity of 99.7% and a thickness of 0.2 mm were cleaned by ultrasonication in ethanol for 3 min and dried in a nitrogen stream. For the anodisation a computer controlled setup consisting of ETSystem SM1600 voltage source and a Keithley 2400 for measuring the current density was used. In order to obtain a higher degree of self-ordering, a two-step anodisation process [29] for the electrochemical preparation of the TiO_2 nanocolumnar layers was used. For this a first anodisation step was carried out for 30 min and the resulting TiO_2 layer was removed by ultrasonication for 5 min in deionized water, leaving a pre-dimpled surface on the metallic titanium substrate. Both anodisation steps were performed in 20 ml of electrolyte containing ethylene glycol, 3 vol.% deionized water and 0.5 wt.% ammonium fluoride (NH_4F) in a two electrode arrangement with the titanium foil as working electrode and a platinum counter electrode (~1 cm^2 area) at applied potentials from 60 V to 140 V. The distance between working and counter electrode was fixed to 1 cm. The second anodisation step was carried out for 1 h. During the anodisation the titanium substrate temperature was set to constant values between −30 °C and +20 °C by a water cooled Peltier element (Conrad electronics). The temperature of the electrolyte was kept constant at room temperature. For immersion investigations nanocolumnar oxide layers were immersed in water for 12 h or directly kept in the

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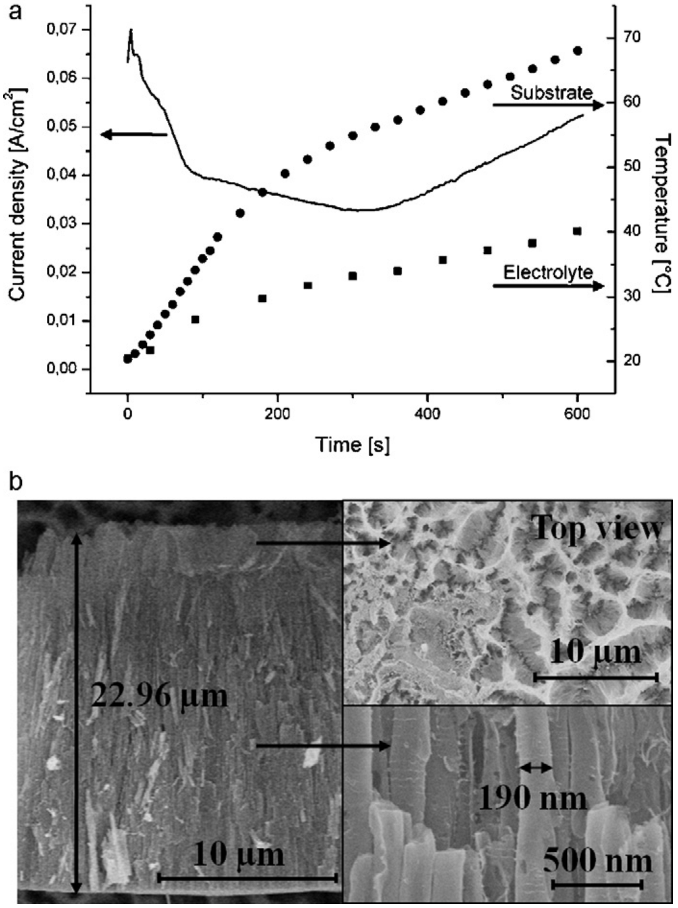

Fig. 1. Anodisation under non-substrate temperature controlled conditions (at 100 V in ethylene glycol, 3 vol.% H_2O, 0.5 wt.% NH_4F). (a) Current density versus time including the corresponding substrate and electrolyte temperature; (b) SEM images (cross-section) of an anodic TiO_2 nanotubular layer grown without substrate temperature control; the upper inset shows the top view and the lower inset shows a high magnification of the nanotubular layer.

electrolyte, without applying a voltage, and heating the substrate to different temperatures (30–60 °C). The morphology and chemical composition of the obtained oxide layers was evaluated using a Hitachi SEM FE 4800 field emission scanning electron microscope (FE-SEM) equipped with an energy dispersive X-ray analyser (EDX).

3. Results and discussion

Fig. 1 summarizes the typical challenges arising upon self-organized anodic growth of TiO_2 nanotubes without using a precise temperature control. Fig. 1a shows the recorded current–time behavior upon anodisation in an electrolyte containing ethylene glycol, 3 vol.% deionized water and 0.5 wt.% ammonium fluoride (NH_4F) at 100 V. The obtained *I*–*t* curve is for the first 300 s in shape and magnitude typical for the anodisation of titanium in fluoride containing electrolytes for establishing the growth of self-organized TiO_2 nanotubes [30]. Roughly the transient can be divided into three sections [25]: (a) high field assisted oxide growth; (b) contribution of fluoride species in the field aided process. In this stage a combination of oxide formation and oxide dissolution takes place, whereas the fluorides cause the dissolution of the formed TiO_2, or the capturing of released Ti^{4+} ions by complexation as $[TiF_6]^{2-}$ [25]. Furthermore the fluorides migrate towards the metal surface, resulting in a fluoride-rich layer at the metal–oxide interface; and (c) diffusion limitation of the tube growth, caused by depletion of reactant species with higher oxide layer thickness and depletion in the nearby electrolyte [31]. In contrast to the ideal case, under the above mentioned anodisation conditions a steady increase in current density after 300 s is observed. The simultaneously measured temperature of the metallic titanium substrate and the electrolyte shows an increase from room temperature to 68.8 °C and 40 °C, respectively. At this point the experiment was stopped to prevent evaporation of the electrolyte.

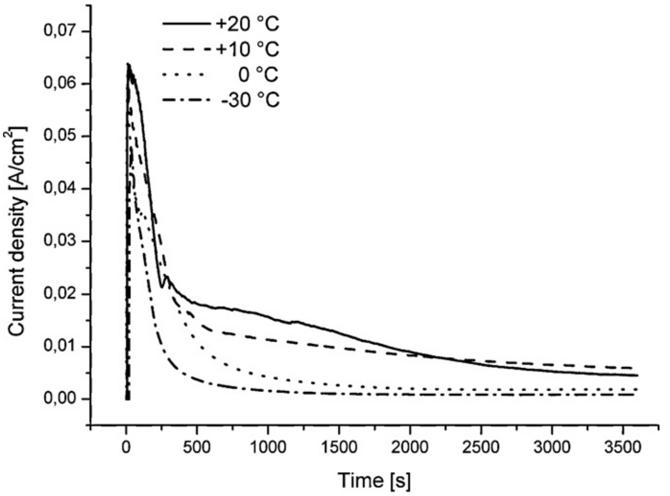

Fig. 2. Measured current density versus time curves (as in Fig. 1), but using precisely controlled substrate temperatures between −30 °C to +20 °. Anodisation in ethylene glycol, 3 vol.% deionized water, 0.5 wt.% NH_4F at 100 V.

Fig. 1b shows a SEM cross-section image of the grown TiO_2 nanotubes, which have a mean diameter of 190 nm and a length of about 23 µm, yielding a formation rate of 2.3 µm/min. Under these conditions the nanotubular layer undergoes intense chemical etching, resulting in roved nanotube endings described as nanograss in literature [32], as apparent in the upper inset. This effect is accelerated by the increasing temperature. In order to counteract the increase of temperature during anodisation, control over the substrate temperature and electrolyte temperature was established as described in Section 2.

If these controls are in place, *I*–*t* curves for the same experimental conditions as in Fig. 1 can be obtained at different substrate temperatures as shown in Fig. 2. As no run-off increase of current densities occurred anymore, the anodisation durations were extended to 1 h. In general, the current densities decrease with decreasing the temperature.

Fig. 3 shows SEM images of the obtained layers formed at constant substrate temperatures of 20 °C to −30 °C.

At a controlled substrate temperature of 20 °C (Fig. 3a), nanotubes with the same outer tube diameter (as in Fig. 1), but a significantly smaller inner pore diameter and thick tube walls can be observed. Although the anodisation time was six times higher than in the non-controlled case, the length of the nanotubes accounts to 11.5 µm. This is in line with a recent report of Enachi et al. [33], who observed thicker tube walls with lower temperatures. This effect is attributed to the double wall morphology of TiO_2 nanotubes when formed in most organic electrolytes [34,35].

In the case of a substrate temperature that is decreased to +10 °C, a highly ordered hexagonal shaped nanocolumnar morphology (Fig. 3b) can be observed. In contrast to already known anodic TiO_2 morphologies in literature, these structures do not show an inner pore at all. The outer diameter of the nanocolumns accounts to about 190 nm and a length of about 7 µm.

At substrate temperature of 0 °C (Fig. 3c), a two-layered oxide structure can be observed in the cross-sectional view. On the top a