Materials Letters 142 (2015) 97–101

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Anodized TiO_2 Nanotubes: Effect of anodizing time on film length, morphology and photoelectrochemical properties

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ARTICLE INFO

Article history:
Received 13 October 2014
Accepted 27 November 2014
Available online 4 December 2014

Keywords:
Anodization
TiO_2
Nanotubes
IPCE
Photoelectrochemical Water Splitting

ABSTRACT

The influence of anodizing time on the length, morphology and photoelectrochemical properties of TiO_2 Nanotubes (NTs) has been investigated. An optimum anodizing time of 20 min at 30 V leads to 1.1 μm long NTs films, generating a photocurrent density (J_{photo}) of 460 $\mu A/cm^2$. Anodized films grown for a time shorter than 10 min show only a thin (100 nm) porous layer, instead of well-defined NTs, and exhibit lower photocurrent densities. Similarly, J_{photo} is lower in NTs grown for 1–2 h, partly because the NTs are damaged after extended anodization and partly because their length (l) already exceeds the electron diffusion length (L_n), found to be 0.8 ± 0.1 μm. The Incident Photon to Current Efficiency (IPCE) study reveals how the microstructural changes (morphology and length) affect the behavior of the anodic films over the photoaction spectrum. IPCE analysis confirms the superiority of 1.1 μm long and well-defined NTs, with a maximum value of 18% recorded at 340 nm. In contrast, the ability to collect electrons decreases for longer and partially damaged NTs, especially in the region 360–300 nm. A small response above 400 nm is observed in all the photoelectrodes, due to oxygen vacancies induced during annealing.

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1. Introduction

Anodized TiO_2 Nanotubes (NTs) [1,2] have received wide attention from the research community over the last decade, as they are relevant in dye sensitized solar cells [3], photocatalysis [4], biomedicine [5] and gas-sensing [6]. The (photo) electrochemistry of TiO_2 NTs is a fascinating and key topic to study in order to optimize the performances in the aforementioned fields [7]. Concerning the solar water splitting process, an electron diffusion length (L_n) of 24 μm is reported for smooth NTs, although in the presence of a sacrificial agent [8]. The presence of long-lived electrons in TiO_2 NTs, indicating excellent charge carrier lifetime and potential for efficient electron transfer and transport, is also confirmed by time resolved spectroscopy studies [9]. Beranek [10] reported that the highest photocurrent gain with the NTs is achieved at a relatively low bias because the maximum space charge layer (W) generated within such nanostructure is limited by the NTs' wall thickness. In contrast for compact semiconductors the photoresponse follows the Gärtner model [11] and keeps increasing proportionally to the applied bias. Despite the intensive research efforts on TiO_2 NTs, Paramasivam [4] argued that a more quantitative survey on the influence of tube morphology, length, wall thickness and tube diameter is needed to better understand their photoelectrochemical properties. Likewise, Augustynski [12] underlined that the assessment of the photoelectrochemistry of TiO_2 NTs is made difficult by the lack of systematic data, particularly those showing how their length affect the Incident Photon to Current Efficiency (IPCE) over the photoaction spectrum.

Aim of the work: The aim of our work is to evaluate the effect of anodizing time on the length, film morphology/microstructure and photoelectrochemistry of undoped TiO_2 NTs. The investigation helps to understand what is required to develop an anodic film with an optimized photoresponse. An often neglected aspect is the significant impact of the anodizing potential on the semiconducting properties of TiO_2 NTs [13,14]; to minimize changes in the electronic properties of the anodic films, a constant anodizing potential of 30 V has been utilized within our study. The solar water splitting process [15] is chosen as a model reaction.

2. Experimental methods

(i) *Anodization.* Prior to anodizing, the Ti specimens (Ti 99.6%, Goodfellow, Cambridge Limited, 0.5 mm thick) were mechanically grinded with SiC paper and ultrasonically cleaned for 10 min in isopropyl alcohol. Anodization was carried out in a two

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http://dx.doi.org/10.1016/j.matlet.2014.11.145
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electrodes cell, applying a potential of 30 V (power supply: Keithley 2450) between the Ti anode and a Pt cathode and varying the anodizing time (5 min–2 h). The electrolyte consisted of 75 ml of anhydrous Ethylene Glycol (Sigma-Aldrich), 3 ml of distilled H_2O and 0.3 g of NH_4F (Sigma Aldrich). As-prepared anodized samples were rinsed with water, ultrasonically cleaned with ethanol and stored in ethanol overnight. The amorphous specimens were converted to anatase at 450 °C [16,17] in air (heating rate: 100 °C/h, dwelling time: 1 h, furnace type: LHT 04/17, Nabertherm).

(ii) *Morphology*, *Microstructure* and *Crystallinity*. The photoelectrodes were analyzed by a Field Emission Nova NanoSEM 230 (Nova FEI). Crystal phases were measured by Grazing Angle X-Ray Diffraction (GAXRD, geometry, $\omega = 1°$), using a Panalytical, X'Pert Pro instrument (Cu-Kα1, $\lambda = 1.5406$ Å).

(iii) *Photoelectrochemical Characterization*. The photocurrent measurements were performed with a Voltalab80 PGZ-402 (Radiometer Analytical) potentiostat, with a TiO_2 NTs Working Electrode (WE), Pt plate (XM120, Radiometer Analytical) Counter Electrode (CE) and Ag/AgCl/3M-KCl (XR300, Radiometer Analytical) Reference Electrode (RE) fitted in a Cappuccino Cell [18] filled with 10 ml of 1 M KOH. A potential sweep from −900 to +700 mV was applied to WE vs RE (scan rate of 20mV/sec). The WE was irradiated by a Xe lamp (solar simulator L.O.T–Oriel AG), at an intensity of 80 mW/cm^2 and the resulting photocurrent density (J_{Photo}) was recorded. Incident Photon to Current Efficiency (IPCE) analysis was performed using a Xe lamp (L.O.T–Oriel AG) and a monochromator (Omni-λ 300, L.O.T–Oriel AG). The TiO_2 NTs photoanodes, immersed in 1 M KOH, were irradiated by different wavelengths (λ) ranging from 550 to 280 nm, while a potential bias of 0.23 V (Keithley 2450) was applied between WE and CE. The resulting current was measured as a function of λ, $J_{Photo}(\lambda)$, and used to calculate the IPCE.

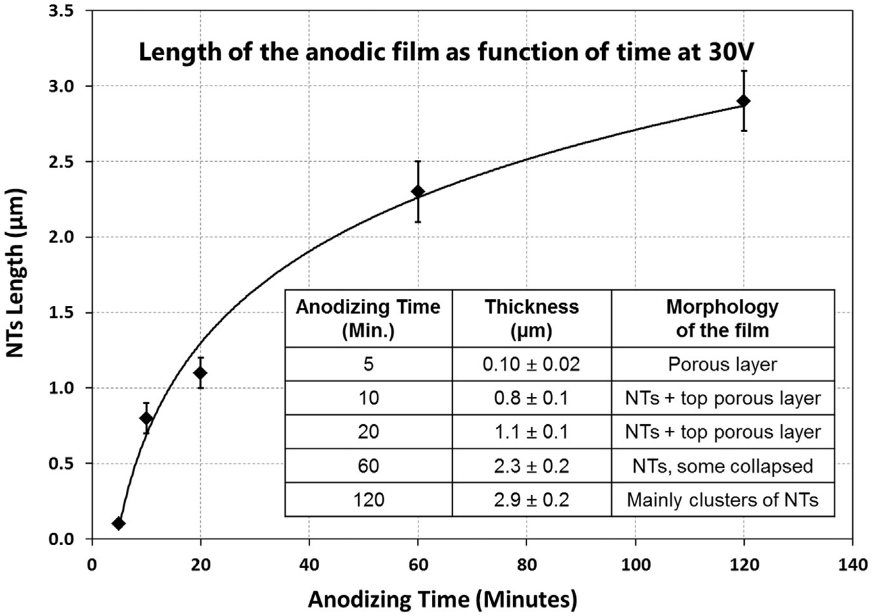
3. Results and discussion

Fig. 1 illustrates how the morphology of the anodic layer evolves and the length of the NTs film increases with the anodizing time. After 5 min the anodic film is 100 ± 20 nm thick and rather than well-defined NTs, only a porous layer can be seen (Fig. 2a). NTs are instead clearly visible after 10 and 20 minutes (Fig. 2b and c), their length being respectively 0.8 ± 0.1 μm and 1.1 ± 0.1 μm; the top of the NTs is mostly covered by an initiation porous layer [19], a common scenario in organic electrolytes (Fig. 2b, c). However the mouth of the NTs is free of this porous layer in some parts of the film, as shown in the inset of Fig. 2c. The anodic NTs can grow longer (~3 μm) by extending the anodizing time further, as shown in Fig. 2d, e, although the top of the NTs is gradually destroyed. Indeed, the partial collapse of the NTs due to over-dissolution of the top of the tubes can already be appreciated after 1 h (Fig. 2d) and becomes very significant after 2 h (Fig. 2e), leading to the formation of spikes [20] or clusters of NTs and therefore to a substantial change in the morphology of the anodic film.

The GAXRD spectra of the TiO_2 NTs are shown in Fig. 3. As-prepared NTs are amorphous and converted to anatase following the thermal treatment at 450 °C [16]. Clearly, as the NTs grow longer, TiO_2 peaks become more significant than peaks belonging to the Ti substrate underneath the oxide. As the crystal phase (anatase) does not depend on the anodizing time (Fig. 3), any difference in the photoelectrochemical response of the films can be ascribed to the different lengths (l) of the NTs and changes within their microstructure/morphology.

The photoelectrochemical analysis of the anodic films is summarized in Fig.4a, b. The thin porous layer obtained after 5 min anodization behaves differently than films grown for a longer time (10–20 min) and having well-defined NTs. Its poor J_{Photo} in comparison to NTs grown for 10 min, particularly evident at negative bias (−0.8 to −0.4 V vs Ag/AgCl), suggests that after 5 min the anodic film is far from an optimal photoresponse, both in terms of morphology and length. Such a thin film resembles the behavior of a compact layer and its J_{Photo} does not saturate, but increases proportionally with the applied bias [10,11].

A different scenario is observed once well-defined NTs are formed; J_{Photo} at 0.0 V vs Ag/AgCl (1.0 V vs RHE) raises from 360 to 460 μA/cm^2 by increasing the anodization time from 10 to 20 min. More importantly, the J_{Photo} at negative bias (−0.8 to −0.4 V vs Ag/AgCl) is significantly improved in comparison to 5 min growth, providing a direct evidence for the lower charge carrier recombination occurring in well-formed NTs, which may be ascribed to a directional charge transport (i.e. 1D transport) within the tubular structure. The photoresponse then decreases to 320 and 300 μA/cm^2 (at 0.0 V vs Ag/AgCl) when extending the anodization time to 1 or 2 h, respectively (Fig.4a). This suggests that the optimal length has been exceeded (l is 2.3 μm at



Anodizing Time (Min.)	Thickness (µm)	Morphology of the film
5	0.10 ± 0.02	Porous layer
10	0.8 ± 0.1	NTs + top porous layer
20	1.1 ± 0.1	NTs + top porous layer
60	2.3 ± 0.2	NTs, some collapsed
120	2.9 ± 0.2	Mainly clusters of NTs

Fig. 1. The NTs thickness vs anodizing time plot shows that the NTs are ~1 μm after 20 min at 30 V. Within the explored time range (up to 2 h), the maximum thickness was ~3 μm.

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