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Tailoring anatase nanotubes for the photovoltaic device by the anodization process on behalf of microstructural features of titanium thin film

V. Mandić[a,*], M. Plodinec[a], I. Kereković[a], K. Juraić[a], V. Janicki[a], D. Gracin[a], A. Gajović[a], A. Moguš-Milanković[a], M.G. Willinger[b]

[a] *Ruđer Bošković Institute, 54 Bijenička cesta, HR-10 000 Zagreb, Croatia*
[b] *Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, D-14195 Berlin, Germany*

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ABSTRACT

We prepared the anatase nanotubes (NT) and other nanostructured titania as electron accepting/transmitting layers in solar cells, using titanium anodization. Upon gaining control over the anodization, the parameters were held constant in order to observe the role of the deposited layers (by electron beam evaporation and magnetron sputtering) on the NT yield. The structural and microstructural parameters were investigated using FIB-FEG-SEM, XRD, Raman and GIXRD. Differences in the titanium layers play a significant role on the type of titania nanostructures achieved. Only dense homogeneous titanium layer surface, uniform in thickness and without cracks at macroscale, with uniformly seized isotropic nanoparticles, will enable uniform electrochemical etching and thus favourable, reproducible formation of the titania NT, and upon thermal treatment the anatase NT. Transparent conductive oxide (TCO) layers, which are not in direct contact to the NT, can also exhibit influence on the morphology of the titania NT charge transfer layer. In order to reach large uniform areas of nanotubes, which is required for solar cell application, the preparation of titanium layer has to be tailored.

1. Introduction

Photovoltaic devices seem to be the most lucrative answer (clean, free, unlimited, low maintenance, etc.) to the large demands of the future [1]. In a 3rd generation photovoltaic device, like dye sensitized solar cell (DSSC), or perovskite based solar cell (PSC), electron transmitting material (ETM) layer is considered to be the curtail for enabling high efficiency in the overall performance of solar cell [2,3]. Namely, when excited by the light, active material will yield excitons and the electron transmitting material which is underlaying the active material will ensure separation of the charge carriers and their further transfer to the electrode in order to finally yield electricity. The better the process, the higher performance of overall solar cell is achieved. The problem lies within the short lifetime of the photogenerated charge carriers, therefore the layer has to remain thin. Implementation of various nanostructural forms of the buffer layers ensures the increase of specific surface area, and enables more efficient charge transfer without the need to increase the thickness of the layers. Majority of non-inverted solar cells (SC) repose on the transparent conductive oxide (TCO) layer in order to serve as a transparent electrode underlying the electron transmitting material. Actually, the interface between the overlaying charge transfer oxide (CTO) layer and the underlaying transparent conductive oxide (TCO) layer is concerned as one of the critical parameters in active material-to-electrode electron transport. The main disadvantageous process in the solar cells is the non-radiative recombination which is more probable at the interfaces of grains in the active material, but will also occur at the defect states in bulk of the active materials. Having in mind a multi-layer assembly of a solar cell, limits in the control of the interfaces can be nominated as one of the main reasons why nowadays all (familiar) types of solar cell (SC) materials still fail to get closer to the theoretical efficiency limits.

While literature agrees that the most important task is the optical, electrical and structural compatibility of active and passive layers, there is no consensus on mechanisms of processes at boundaries (for example charge transfer, charge recombination, etc.) which cause discrepancies in optimisation efforts [1–22]. Thus, in the bottom-top solar cell assembly processes, much attention is devoted to the strategy of overlaying the CTO layers. The upgrade in efficiency of modern solar cell is known to depend not only on the chemical composition of the active material but also significantly on the morphology of materials at the interface between active and transport layers. Having in mind the chemical composition, titania is recognised as photoactive, photocatalytic, semiconducting material with known application as both charge transfer and active absorbing material [4]. In the case of special

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* Corresponding author.
E-mail addresses: vmandic@irb.hr, vmandic@fkit.hr (Vilko Mandić).

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morphology, i.e. tailored self-organisation, for the titania thin films one can expect very favourable charge transfer properties, for example in the case of titania nanotube based thin films [5]. Such thin film can show significant enhancement of solar cell properties when used as an electron transmitting material, i.e. when placed between the absorbing material and the conductive transparent oxide layer, i.e. electrode. When compared to a nanoparticle film, TiO_2 nanotubes (NT) have a large area-to-volume ratio, superior lifetime and provide optimal pathways for electron percolation, thus the ability to produce ordered self-assembled anatase nanotubes presented a huge milestone [6]. A 25% increase in the charge collection efficiency of nanotube-based solar cell when compared to nanoparticle-based solar cells occurs due to the enhanced light scattering and slower electron recombination [7]. Namely, morphology and self-organisation of CTO ensure enlarged specific surface area, i.e. contact to active material, while CTO remains thin enough to overcome the problem of the short lifetime of photogenerated charge carriers. The use of various nanostructural forms of inorganic materials in different crystal sizes in hybrid solar cells may allow additional tuning of the optical and electrical properties. The literature nominates various nano structures like tubes, rods, wires, fibers, particles, etc. [8]. Furthermore, tailoring of the optical gap and surface chemistry is employed to enhance the transfer of photogenerated carriers towards the external circuit. Currently, efficiencies of up to 13% were achieved for the titania NT-based DSSC, while above 20% for the NT-based PSC [9,10]. It is important to point out that these materials are the most cost effective solar cell constituent layers, both in terms of material and preparation (both laboratory and scale up) costs vs. power conversion efficiency. Subsequently, all of the above-mentioned influence the efficiency/stability of SC.

Layer deposition techniques also play an important role in the previously mentioned high efficiency separation of charge carriers and their transport from the absorbing material to the electrode. Achieving affordable and reliable deposition technique is the continuous matter of scientific effort [11–15]. Preparing the titania nanotube layer reposes on the starting Ti-layer. The successfulness of Ti deposition (with respect to structure, morphology, thickness, particle size, uniformity, etc.), anodization (with respect to deposition parameters), and thermal treatment (with respect to anodization parameters) is a necessity for the homogeneous surface which is needed for the solar cell application. In this case, a fully controllable and reproducible preparation procedure on all type of substrates still presents a challenge [16–18]. Namely, the Ti anodization process was introduced as a convenient way to produce the TiO_2 NT with various geometries in terms of nanotube length, diameter and wall thickness (basically a electrochemical etching process of the titanium in the ammonium fluoride electrolyte solution of various concentrations under different currents, where intermediate titanium fluoride is dissoluted to form amorphous titania nanotubes) [19–29], whereas the subsequent thermal treatment is required to promote the crystal transformation to anatase [30]. The process depends on many parameters, such as the F^- ion concentration [31,32], the type of solvent [33], temperature [34,35], stirring [36] and anodization potential [34,37]. Yet anodization voltage and ammonium fluorite solution concentration are nominated as the most important. By changing these parameters, the nanotube parameters can be controlled, i.e. inner and outer tube diameters and the wall thickness [25]. The easiest way to control the length of the tubes is through the duration of the anodization process [38,39]. Very low water content in polar organic solvents may considerably decrease the rate of chemical dissolution and thus increase the nanotube length [40,41]. The presented anodization process was generalised as simple and facile. Namely, it was usually performed on commercial titanium foils. Such titanium materials were usually homogeneous with well-defined morphologies. XRD of such material yields the titanium with hexagonal crystal lattice. The need to produce the anatase nanotubes on different substrates, like the transparent substrates, brings about the problems in their preparation in micro- and macroscopically uniform manner [42]. In the literature, much attention is dedicated to the geometry of anodization derived TiO_2 NT layers, as it is presumed it is mainly responsible for the solar cell performance efficiency. The use of anatase nanotubes in solar cells is known to be more favourable in the non-inverted setup, meaning the light enters the cell on the titania side. Common substrate that ensures mechanical strength for the cell and transparency is glass. On top of glass one should have transparent electrode. For a transparent conductive oxide layer, aluminium doped zincite (AZO) is commonly used. Alloy of indium tin oxide (ITO) and fluorine doped tin oxide (FTO) are renowned candidates as well. In order to produce the nanotubes, it is necessary to deposit a thin film of titanium on top of TCO layer. Understanding of the transport mechanisms in titania nanotubes (with respect to their geometry), as well as the reproducibility of the preparation process (on all type of substrates) are still a matter of controversy and act as a milestone in the future upgrade of the titania NT-based solar cell performance [18,39].

In this work, the influence of titanium layer (structure, morphology, uniformity, thickness, etc.) deposited on the TCO layer, on formation of well-defined homogeneous, ordered, self-organised, self-standing titania nanotubes was studied in terms of the morphology of achieved nanotubes and reproducibility of the anodization process. The use of various nanostructured arrays may allow additional tuning to ensure the overall compatibility of all layers. The controlled deposition of the starting titanium layer was shown to be a prerequisite for successful anodization. The results of this work show that interface properties of layers underlaying the derived titania nanotubes (TCO, Ti) may significantly attribute to the behaviour of the solar cell.

2. Experimental

2.1. Synthesis parameters

The syntheses of porous TiO_2 structures or TiO_2 nanotubes by the anodization process were performed on Ti layer deposited by electron beam evaporation or magnetron sputtering under marginally different conditions on glass substrate with TCO layer. Thereafter, the prepared titanium samples were microstructurally and structurally characterised. Subsequently, the titanium thin films were anodized to titania nanotubes and thermally treated to anatase nanotubes (all under the same conditions) (Fig. 1) and then microstructurally and structurally characterised again. The only process parameters that were differed are brought up in Table 1. Few steps were performed during the preparation:

Glass substrates with transparent conductive electrode (aluminium zincite – AZO, Aldrich, United Kingdom; indium tin oxide – ITO, Ossila, United Kingdom; fluorine tin oxide – FTO, Aldrich, United Kingdom) for the depositions of titanium had to be cleaned. The cleaning procedure includes 3-step washing in ultrasonic bath cleaner (US) in: (i) detergent, (ii) acetone, (iii) ethanol, and subsequent boiling in MilliQ H_2O.

Electron beam evaporation (EBE) for the titanium deposition was performed in a modified Varian 3117 chamber, where parameters

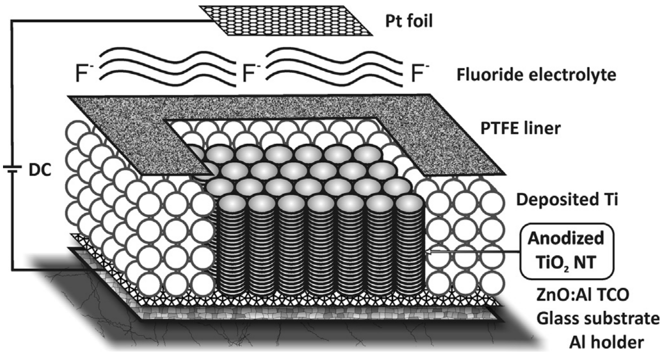

Fig. 1. Scheme of the anatase nanotubes preparation by titanium anodization.