OPEN TOP AND SELF-ORGANIZED LONG TITANIUM DIOXIDE NANO TUBES PREPARED BY ANODIZATION OF SPUTTERED TITANIUM LAYER

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Abstract

Anodization is a simple and effective method to synthesize self-organized titanium dioxide nanotubes. But depending on the electrolyte used for anodization, there is a disorder “nano grass” or an “initiation layer” on top of the nano tubes. Additionally peeling off the nanotubes from substrate might happen during the anodization of titanium which is sputtered on the fluorine doped tin oxide (FTO). Removing this unwanted layer (without delamination), especially in high length TiO_2 nanotubes could increase the photo electrochemical performance. Here we report a novel method to anodize the titanium layer homogenously and to produce open top nano tubes. Results show that the photo current density of samples will be increase up to 15 % after opening the top surface of nanotubes.

Keywords: Open top TiO_2 nano tubes, anodization, nano grass, initiation layer, sputtering

1. INTRODUCTION

Titanium dioxide (TiO_2) is a well-known semiconductor for its photoelectrochemical properties and it is used for instance in perovskite solar cells (PSCs), dye sensitized solar cells (DSSCs) [1,2], water splitting [3] and photocatalysis [4]. One dimensional nanostructures such as nanotubes, provide a straight pathway for photogenerated electrons and could increase the efficiency of such devices [5]. Anodization is a simple method for producing self-organized TiO_2 nanotubes. Fluoride contained electrolyte like HF or NH_4F solution is necessary for growth of TiO_2 nanotubes. However, in both cases long TiO_2 nanotube films grown by these solutions are always covered by a grassy top layer [6] or initiation layer [7]. This disorder top layer can significantly reduce the efficiency of charge transfer [7-9]. Therefore, long TiO_2 nanotubes with open and clean top surface are highly desirable for electron-transport applications such as solar water splitting, PSCs and/or DSSCs. In addition, in these applications it is desirable to illuminate TiO_2 nanotubes from both back and front sides [5]. Therefore, growing TiO_2 directly on a transparent conductive charge collecting layer such as fluorine doped tin oxide (FTO) by the electrochemical anodization of magnetron sputtered titanium on FTO is highly favorable. Preparation of TNTs from the sputtered titanium films without peeling off requires homogenous anodization.

In order to obtain the open top TiO_2 nanotubes several approaches have been proposed, including producing different polymorph of TiO_2 at the top and removing it after anodization [8], resistant layer technique [7] and multi-step anodization [10]. All these methods produce open-top TiO_2 nanotubes. But all of these methods produce open top TiO_2 nanotube layer which were grown on pure Ti or Ti alloy films.

Here we proposed two step anodization with optimized conditions to remove the as-anodized disorder top layer easily and effectively in long length TiO_2 nanotubes which were grown directly on FTO glass. These technique consist of growing a weak and non-sticky layer at top surface of nanotubes as sacrificial layer and then removing this layer by sonication. Furthermore, we proposed a simple technique to produce homogenous and highly adherent TiO_2 nanotubes directly grown on FTO substrate. By using this technique, it is possible to synthesize TiO_2 nanotubes with length up to 20 µm.

2. EXPERIMENTAL

2.1. Deposition of Ti-Ta thin film on ultrasonically cleaned FTO

The stainless steel plasma reactor used in this work is equipped with a 4 inch magnetron sputtering unit and a stepper motor controlled rotatory substrate holder with a heater. For the deposition of the titanium tantalum composite, a titanium 4 inch target of 99.99 % purity with a tantalum wire of diameter 0.05 mm at the center of the Ti target is fitted in the magnetron source. Ultrasonically cleaned (subsequently in acetone, ethanol and deionized water for 5 minutes each) and nitrogen dried FTO glass is used as substrates for titanium tantalum alloy film deposition. The plasma reactor is pumped down to the base pressure of 5×10^{-5} Pa by means of turbo molecular pump in combination with a rotary pump. A RF plasma cleaning of the FTO glass substrates is carried out at pressure 15 Pa in argon plasma (100 sccm) at -120 V self-bias by applying 13.56 MHz RF 50 Watt. Afterwards, an adhesion treatment is performed by a separate plasma treatment in presence of forming gas (mixture hydrogen and nitrogen) and argon (flow 10 sccm each) at pressure 15 Pa and self-bias -120 V by applying RF 13.56 MHz power 45 Watt. Then, working pressure 0.2 Pa is achieved by introducing 15 sccm argon gas and controlling the gate valve. At the working pressure sputtering is carried out by pulsed DC power supply at frequency 50 kHz with duty cycle 50 %, power ~ 700 watt, discharge current ~ 630 mA and discharge voltage ~ 1120 V for 145 minutes without intentional substrate heating.

2.2. TiO_2 synthesize

TiO_2 nanotubes were synthesized at room temperature via electrochemical anodization. **Figure 1** shows the setup that used for anodization. The thickness of sputtered layer varied from 2.2 μm up to 7 μm. Two different solutions were used as electrolyte. The first one was HF (0.2 M, Sigma Aldrich), ethylene glycol (Sigma Aldrich) and distilled water (4 wt. %) and the second one was NH_4F (0.15 M, Sigma Aldrich), ethylene glycol (Sigma Aldrich) and distilled water (3 wt. %). The surface of the sample was connected to the positive terminal of power supply as anode and 1 cm^2 platinum sheet with 1 mm thickness was connected to the negative terminal as the cathode. In case of HF electrolyte, the voltage was set to 120V (D.C.) and in case of NH_4F electrolyte the voltage was set to 20V (D.C.) for the first step anodization (10 min) and 70V (D.C.) for second step anodization. The vertical distance between anode and cathode was kept constant in about 1.5 cm. In all cases the anodization continued until the consumption of all Ti-Ta layer. After anodization the samples was rinsed with ethanol and dried in nitrogen stream immediately. The samples was finally annealed at 450°C for 3h in air atmosphere with heating and cooling rate of 2°C/min.

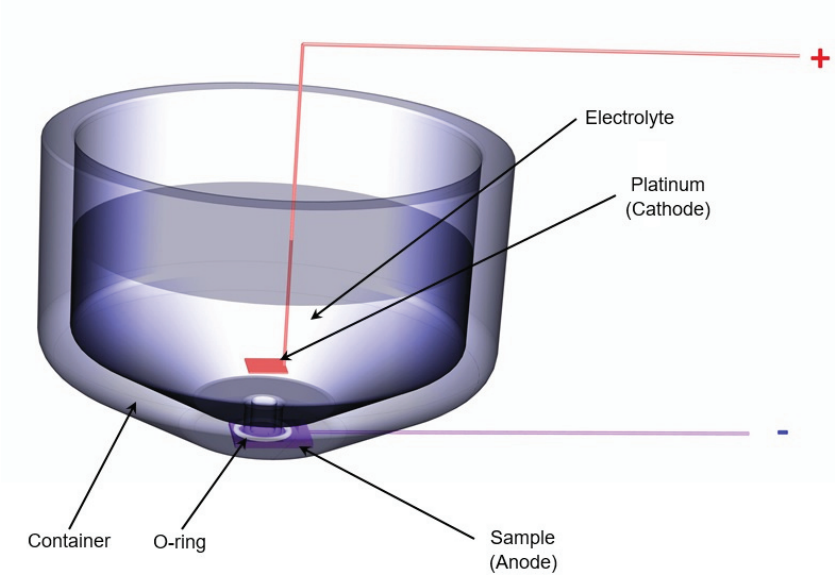

Figure 1 Anodization setup

2.3. Sample characterization and measurement

The morphology of the top surface and thickness of the TiO_2 layer after anodization were measured using scanning electron microscope Hitachi SU6600 (Hitachi, Tokyo, Japan). The thickness of the films before anodization were measured with the help of profilometry. X-ray diffraction patterns were recorded at room temperature with an Empyrean (PANalytical, The Netherlands) diffractometer in the Bragg-Brentano geometry, Co-K_α radiation (40 kV, 30 mA, λ = 0.1789 nm). The photoelectrochemical data were collected using a standard three-electrode electrochemical cell with a Gamry Series G 300 Potentiostat (Warminster, PA, USA). The TiO_2 nanotubes served as working electrode (photoanode), the Ag/AgCl (3M KCl) as the reference electrode and the Pt wire was used as the counter electrode. A 150 W Xenon lamp coupled with an AM1.5G filter was used as a light source. The power intensity was kept at 1 sun (100 mW/cm^2) which was calibrated through a silicon reference solar cell (Newport Corporation, Irvine, CA, USA). The photoelectrochemical behavior of the prepared electrodes was investigated by means of sweep voltammetry measurement in 1M NaOH electrolyte (pH= 13.5).

3. RESULTS AND DISCUSSION

Figure 2 shows the surface of samples anodized with HF and NH_4F solutions. In samples anodized with HF solution, some nanograsses are obvious in the top surface of nanotubes. These nanograsses are formed due to etching of the walls of TiO_2 nano tubes during long duration anodization [11]. The wall thickness of top part of nanotubes become too thin to withstand against their own weight and during drying they will bend and collapse. In the case of NH_4F solution, at the initial step of anodization, a typical initial current spike is present that results in a compact oxide layer on the Ti surface according to a high field oxide formation mechanism [7].

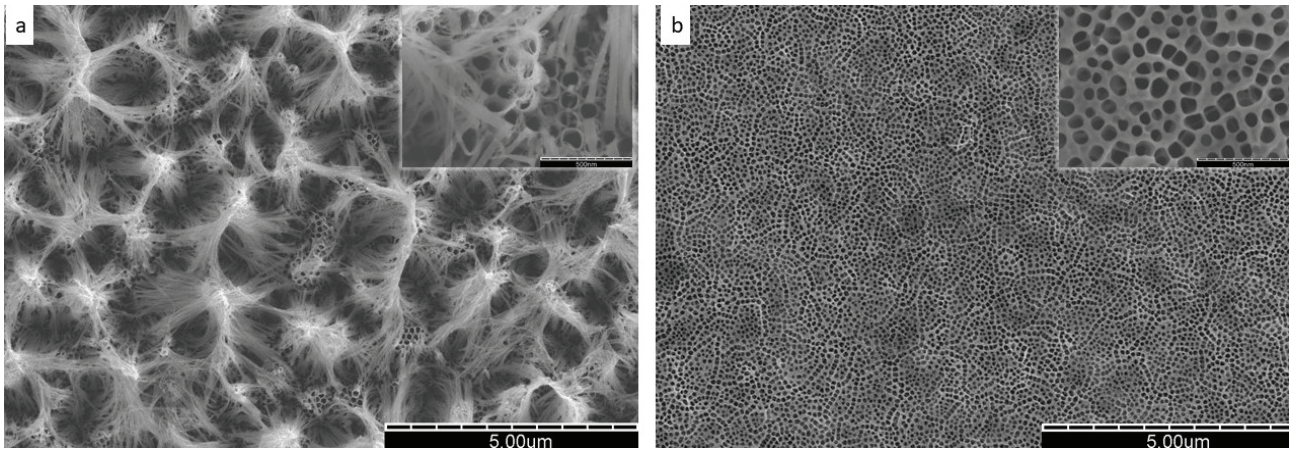

Figure 2 SEM images of top view of samples anodized with a. HF solution (nanograss) and b. NH_4F solution (initiation layer)

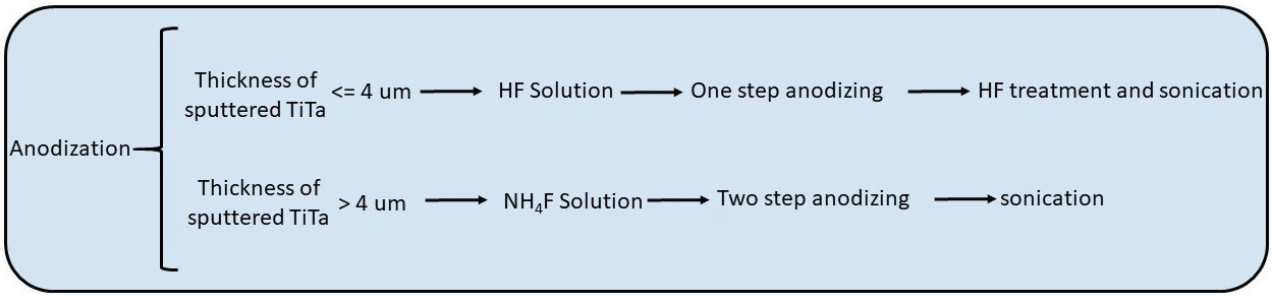

Figure 3 Anodization protocol for samples with various initial thickness

To clean these disorder top layers, we proposed a protocol for anodization of sputtered Ti layer on FTO glass with thicknesses from 2.2 µm up to 7 µm (**Figure 3**). Since TiO_2 easily dissolves in HF, for samples with initial Ti thickness more than 4 µm, the final thickness of TiO_2 does not increase more than 10 µm. Therefore we find that in order to synthesize TiO_2 nanotube with length more than 10 µm, it is better to use NH_4F solution as electrolyte for anodization.

For samples with thickness less than 4 µm, HF solution produce grassy top layer that can be removed by sonication in dilute HF solution in water for maximum 4 minutes (**Figure 3**). Removing the initiation layer is not as easy as in the case of nanograsses. Generally, double step anodization is an effective way to eliminate this layer. During the first step a sacrificial layer grows at the top and by second step, the main layer grows at the bottom. The initiation layer vanishes by removing the sacrificial layer with sonication in water for 4 min (**Figure 4**).

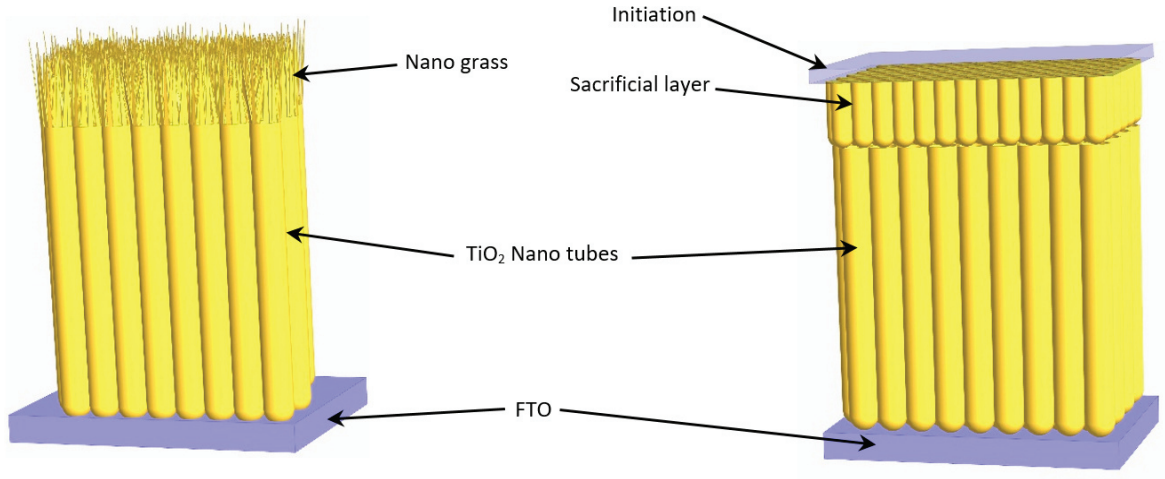

Figure 4 Schematic of nano grass, sacrificial layer and initiation layer

Figure 5 shows the top view of samples after surface treatment with open top nanotube. These open top nanotubes could increase the dye loading in case of dye sensitized solar cell applications. The maximum length of nanotubes that can produce with this technique is around 20 µm.

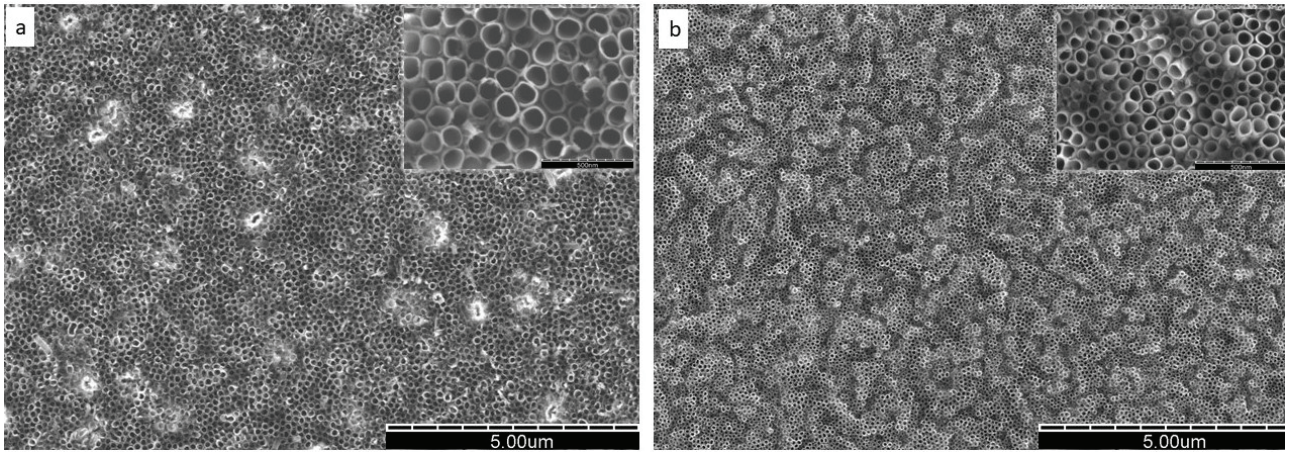

Figure 5 SEM images of top view of samples after surface treatment with a. HF solution and b. NH_4F solution

Photocurrent measurements for sample with about 10 µm thickness before and after surface treatment are shown in **Figure 6**. Cleaning the top surface results in about 15 % increase in photocurrent at 0.6 V (from 40

μA/cm² to 46 μA/cm²). The nano-grasses inhibit smooth electron transport in one direction and decrease the photocurrent by increasing the electron recombination [12].

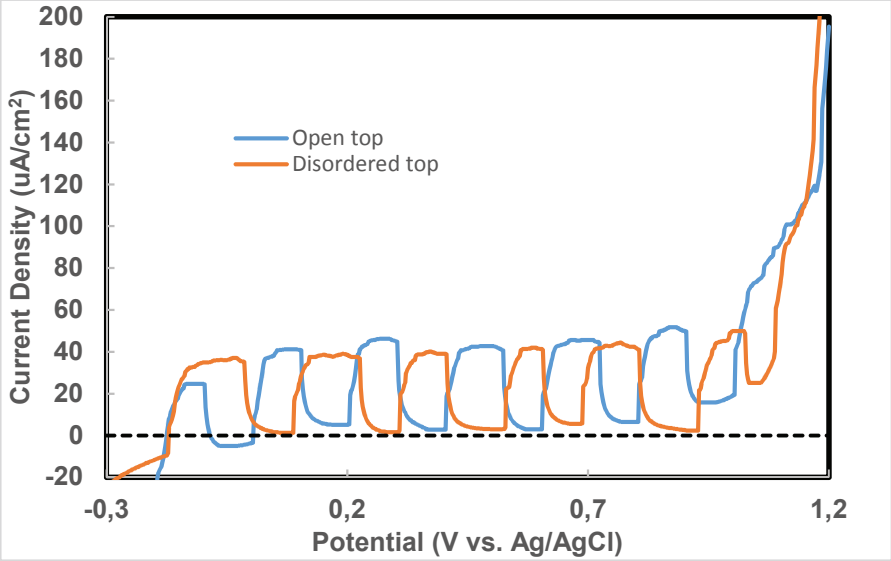

Figure 6 Chopped light polarization curve for TiO_2 nano tubes on FTO glass with open and disorder top, electrolyte 1M NaOH

In order to anodize the Ti-Ta layer homogenously and without delamination, it is necessary to produce completely homogenous conditions for anodization in every parts of the sample. To keep the conditions constant it is necessary to change periodically the position of the cathode (sample) against the anode (platinum) during the anodization without changing the vertical distance between them. By changing the position, every unwanted effects due to inhomogeneity in surface and distance will be distribute in whole part of sample and production of a homogenous anodized surface will be guaranteed. **Figure 7** shows the effect of changing the position of anode during anodization on the homogeneity of anodized sample.

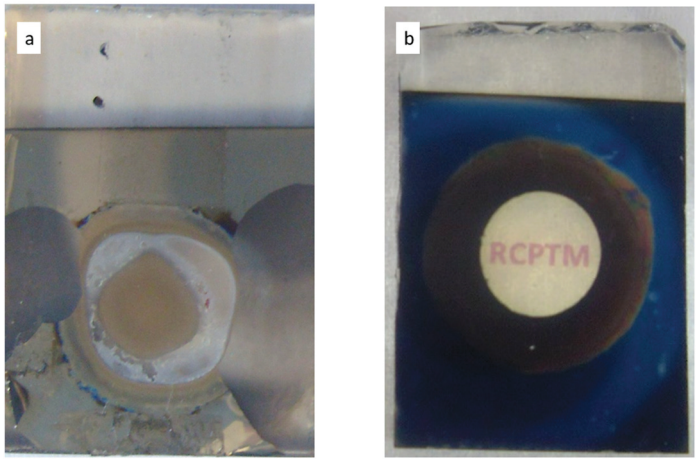

Figure 7 a. Heterogeneous and b. homogenous anodized sample

4. CONCLUSION

Producing open top and long length TiO_2 nanotubes directly on FTO glass is a key factor to fabricate efficient devices like dye sensitized solar cells. In present work we used HF and NH_4F solution to anodize Ti-Ta thin film directly sputtered on FTO. To open the top of synthesized nanotubes with HF solution, we used a simple

surface treatment including HF treatment and sonication in ultrasonic bath. Using NH_4F solution results in initiation layer that could be removed by producing a sacrificial layer at the top of the samples and sonication. These surface treatments result in better photocurrent and will be promising for TiO_2 nanotubes applications.

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