Self-organized formation of short TiO$_2$ nanotube arrays by complete anodization of Ti thin films

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Abstract

We investigate the self-organized growth of short TiO$_2$ nanotubes by complete anodization of Ti thin films deposited on Si substrates in ethylene glycol electrolytes with small addition of NH$_4$F. During the anodization process, real-time inspection of the current transient is performed to anodize the Ti films completely. X-ray photoelectron spectroscopy and scanning electron microscopy are employed to characterize the resulting samples. We find that the length of the formed TiO$_2$ nanotubes is governed by the thickness of Ti thin films independently of the tube diameter. Short TiO$_2$ nanotubes are also found to be stable up to 550ºC in air atmosphere even after crystallization to rutile.

1. Introduction

Recently, synthesis of nanometer-sized TiO$_2$ crystalline materials has attracted considerable attention due to the potential for promising device applications in optics, electronics, photochemistry, biology, energy storage or energy conversion. This is because that the quantum confinement and low dimensionality of these materials gives them unique optical, chemical and electronic properties compared to bulk materials. It is known that a vertically-oriented TiO$_2$ nanotube arrays obtained formed by electrochemical anodization of titanium is one of the typical self-organized fine structures [1]. Extensive research has been also carried out to exploit the functionality of highly-ordered TiO$_2$ nanotubes [2-4].

The morphologic structure of TiO$_2$ nanotubes is of particular importance with regard to their functionality. The increase in length of TiO$_2$ nanotubes offers the possibility of improvement of their photochemical or photocatalytic performance due to the drastic increment of the surface area. Considerable efforts have been made with the fabrication of longer TiO$_2$ nanotubes having a high aspect ratio [5]. On the other hand, it is reported that the...
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electron transport process within the short TiO₂ nanotubes electrode is much favorable compared with that in the long TiO₂ nanotubes [6]. However, there are no reports on the fine control in the length of short TiO₂ nanotubes. In this work, we report on the anodic growth of shorter TiO₂ nanotube arrays by complete anodization of very thin Ti films deposited on Si substrates in ethylene glycol electrolytes with small addition of NH₄F. During the anodization process, real-time observation of the current transient is performed to anodize the Ti films completely without demolishing the nano-architecture. We successfully demonstrate a simple but effective procedure to control the tube length independently of the tube diameter. The annealing and crystalline development of short TiO₂ nanotube arrays are also studied.

2. Experimental

Deposition of Ti thin films was conducted with a dc magnetron sputtering system whose base pressure was 5 x 10⁻⁵ Pa. The substrates used were p-type Si(001) wafers with a resistivity of 1-10 Ωcm. Ti films with a thickness in the range of 50 to 150 nm were deposited at a substrate temperature of 350°C. Electrochemical anodization of Ti thin films was carried out using a commercial potentiostat (Solartron, 1280C) in the electrolyte consists of ethylene glycol containing 0.36 M NH₄F. Prior to anodization, the sample was degreased by sonification in acetone and ethanol, and subsequently rinsed with deionized water, and finally dried in a nitrogen stream. A two-electrode cell was used with a Pt gauge as a cathode/counterelectrode. Samples were contact with an Al back-plate and then pressed against an O-ring in the cell wall, leaving 0.8 cm² exposed to the electrolyte. The anodization temperature was kept at 3°C using an ice bath, in order to prevent the oxide formed from being dissolved in the electrolyte [7]. Chemical characterization was carried out by x-ray photoelectron spectroscopy (Thermo Scientific, VG Sigma Probe) with very shallow take-off angle of a few degrees. Morphological characterization was performed using a HITACHI S-4300 scanning electron microscope (SEM). The crystal phase precipitated in the samples was analyzed by a x-ray diffraction (XRD) measurements (Rigaku, RINT2000).

3. Results and discussion

First, we observe the current transient during the anodization process. The applied anodic potential was initially ramped from 0 to 14 V at a rate of 100 mV/s and then held at 14V. Figure 1 shows the current density versus time of a 150-nm-thick Ti film anodized at 14 V. After an exponential decay within about 100 sec, the current density gradually decreased with time for 500 sec. Previous reports claimed that these behaviors were due to the formation of a barrier oxide and the following growth of pores [8]. A closer inspection of the current behavior in Fig. 1 reveals, as the anodization proceeds, that the current reduces drastically and then it reaches the minimum marked by an arrow.

The anodization of titanium in the fluoride ion containing electrolytes can be ascribed by a competition between the following two chemical reactions [9]:

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\begin{align*}
\text{Ti} + 2\text{H₂O} & \rightarrow \text{TiO}_2 + 4\text{H}^+ + 4\text{e}^- \quad (1) \\
\text{TiO}_2 + 6\text{F}^- + 4\text{H}^+ & \rightarrow [\text{TiF}_6]^{2-} + 2\text{H}_2\text{O} \quad (2)
\end{align*}
\]

Reaction (1) describes the oxide growth at the oxide/Ti interface governed by electric-field aided O²⁻ ion transport through the growing oxide. While a permanent attack of F⁻ ions onto the formed oxide leads to a chemical dissolution of the oxide as soluble [TiF₆]²⁻ complexes according to reaction (2). As the anodization proceeds, therefore, the pores start to grow on the oxide surface and a tree-like growth of nanoporous oxide layers takes place. The Ti film is progressively consumed during the anodization process, and then the current may drastically reduce as the Ti film is anodized completely.

We have also examined a chemical composition of the resulting samples using XPS. Figure 2 shows a depth profile of elements in the sample taken at the point indicated by the arrow in Fig. 1. It should be noted from Fig. 2 that atomic concentrations of oxygen and titanium are 60% and 30%, respectively, at the as-anodized surface. Although the composition of O decreases and Ti increases as the etching proceed, the Ti layer is anodically oxidized completely, as can be clearly seen in Fig. 2. Such a compositional change is attributed to the appearance of reduced
structures by Ar⁺ ion bombardment [10]. Some trace of F detected throughout the film could be attributed to adhesion of [TiF₆]²⁻ species onto nanopores of the oxide surface. Consequently, the morphologic transformation of the Ti thin film into the nanoporous TiO₂ can be achieved by complete anodization of the Ti film on Si without demolishing the nanoarchtitecture.

Next, to confirm the self-organized formation of TiO₂ nanotubes by the above process, morphologic structures are monitored by the taken SEM images. The sample with a 150-nm-thick Ti film has been anodized until the current reaches the minimum and brought out of the electrochemical cell. Figure 3a and 3b shows cross-sectional SEM images of as-deposited and anodized samples, respectively. As expected, the anodized layer exhibits the TiO₂ nanotube arrayed structure with diameter and length of approximately 30 nm and 140 nm. We note here that the thickness of as-deposited Ti film is almost the same as the length of resultant TiO₂ nanotubes, as is clearly observed in Fig. 3a and 3b. We also perform the same anodization process for the Ti film with a thickness of 80 nm and look at the SEM result obtained for the as-anodized sample, as shown in Fig. 4. As can be clearly seen in this figure, as-anodized TiO₂ nanotubes possess a short length of 80 nm. From these results, it is obvious in the complete anodization of Ti thin films on Si that the TiO₂ nanotubes becomes almost the same length as the thickness of Ti films. Comparing two TiO₂ nanotube samples having the different length of 80 and 140 nm [see Fig. 3b and Fig. 4], the tube diameter of those is quite equivalent. The above observations suggest that the tube length of the short TiO₂ nanotubes can be controlled by choosing appropriate thickness of Ti thin films independently of the tube diameter. Our findings may be the first corroboration of a fine control in the length of short TiO₂ nanotubes.

Finally, we evaluate the crystalline development of short TiO₂ nanotubes at elevated temperatures in air atmosphere. The as-anodized TiO₂ nanotubes were found to be amorphous. The TiO₂ nanotubes of 120 nm in length
were annealed at 250, 300 and 550°C under an ambient air for 6 h. XRD patterns of these samples are shown in Fig. 5a. It can be seen from this figure that the sample remained amorphous at 250°C, with the anatase (101) phase appearing at 300°C. The anatase crystallites transform to rutile after annealing at around 550°C. These results are roughly similar to an earlier study in the TiO₂ nanotubes formed on the Ti sheet, which noted that the tubes crystallized in the anatase at about 280°C irrespective of the ambient and the rutile phase appeared at 570°C in humid argon [11]. The thermal stability of short TiO₂ nanotubes is also checked. Figure 5b is an SEM image showing the cross-sectional view of short TiO₂ nanotubes after annealing at 550°C. From Fig.3b and Fig.5b, no difference in the morphologic structure is observed between as-anodized and annealed samples. That is, short TiO₂ nanotubes are robust up to 550°C in air atmosphere even after crystallization to rutile.

**Figure 4.** SEM side-view of TiO₂ nanotubes grown from a 80-nm-thick Ti film anodized at 14 V.

**Figure 5.** (a) XRD θ-2θ scan of the TiO₂ nanotube arrayed layer annealed at 250, 300 and 550°C for 6 h in air atmosphere. (b) SEM side-view of TiO₂ nanotubes annealed at 550°C.

4. Conclusions

We have successfully demonstrated that the self-organized formation of short TiO₂ nanotubes by complete anodization of Ti thin films deposited on Si substrates in ethylene glycol electrolytes with small addition of NH₄F. It was found that the tube length of the short TiO₂ nanotubes can be controlled by choosing appropriate thickness of
Ti thin films independently of the tube diameter. Short TiO$_2$ nanotubes were found to be stable up to 550°C in air atmosphere even after crystallization to rutile phase.

References