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# Formation behavior of anodic TiO<sub>2</sub> nanotubes in fluoride containing electrolytes

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**Abstract:**  $\text{TiO}_2$  nanotube layers can be formed with titanium in the electrolytes containing fluoride by electrochemical method. The role of fluoride ion, the crystallinity of the anodic oxide, and the chemical state were investigated. The results show the anodic film is composed of oxide and a little amount of hydroxide. The presence of  $\text{F}^-$  ions leads to chemical dissolution of Ti oxide layer and prevents hydroxide precipitation. Consequently, chemical dissolution rate increases with increasing the fluoride content in the range of 0-2% (in mass fraction) because  $\text{F}^-$  ions in electrolyte attack the interface and allow the ions of the electrolyte to easily penetrate into the interface. The as-anodized TiO<sub>2</sub> nanotubes exhibit an amorphous structure. Thermally treated nanotubes are composed of mixtures of the anatase and rutile phases.

Key words: TiO2; nanotube; anodization; fluoride

## **1** Introduction

Self-organized nano-scale structures on metals or semiconductors have offered much attention due to the potential applications and the scientific interests. In the past few years, a novel form of valve metal oxide nanostructure has been developed based on anodization. Under specific anodic conditions in electrolytes containing fluoride, highly ordered arrays of oxide nanotubes can grow on various metals such as Ti[1], Zr[2], and W[3]. Particularly, TiO<sub>2</sub> nanotubes formed on Ti have attracted great interests in recent years because of their variety of functional properties and potential applications, such as gas sensing[4], catalysis[5], solar cell[6], and biocompatible materials[7]. As an effective formation method of TiO<sub>2</sub> nanotubes, the anodization process is useful because of low cost and simple fabrication.

In earlier research work, most of  $TiO_2$  nanotubes have been manufactured by anodization in aqueous HF-based electrolytes, but they grew only up to a length of about 500 nm. This limited growth may be assumed to be due to the fast dissolution process of the  $TiO_2$ nanotube layer rather than the formation of an oxide layer by the chemical oxidation process. Recently, the formation of  $TiO_2$  nanotubes in different electrolytes has been reported: aqueous organic solvent, acidic and neutral solution, all of which contain fluoride ions[8]. But, few detailed study has been published for the effect of fluoride in organic electrolytes on the growth of the nanotube. Thus, we studied the formation behavior of ordered  $TiO_2$  nanotubes anodized in glycerin electrolyte containing ammonium fluoride, and the effect of fluoride ion on the nanotube formation and phases of titania with useful physical and chemical properties.

### 2 Experimental

Titanium sheet (99.5% purity) with a size of 3 cm $\times$ 4 cm was cleaned by sonication in aceton, ethanol, and rinsed with deionized water for 10 min. The anodization to obtain TiO<sub>2</sub> nanotubes was carried out in electrochemical cell by using a direct current source at a constant voltage of 20 V. The samples were anodized in mixture of glycerin+water (70:30 of volume ratio) with NH<sub>4</sub>F in the content range of 0–2% (in mass fraction). All electrolytes were prepared with reagent grade chemicals. Titania nanotube array was characterized by FE-SEM, XPS, XRD, etc.

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### **3** Results and discussion

Fig.1(a) shows a top-view image of TiO<sub>2</sub> nanotubes formed at 20 V for 1 h in NH<sub>4</sub>F mixture of glycerin and water (70:30 of volume ratio). Clearly, the anodization results in ordered porous structures with pore opening of approximately 100 nm in diameter. In order to measure the nanotube walls and ripples, TiO<sub>2</sub> nanotubes were separated from the Ti substrate. As shown in Fig.1(b), the nanotubes were connected with each other, and the ripples occurred at sidewall of them after anodization. The origin of these ripples was considered the phenomenon that periodically repeated differences in the dissolution and oxide formation rate cause to leave some parts of the walls thicker or thinner than the other, thus leading to sidewall rippples[9]. The length and average outer diameter of nanotubes were 1 200 nm and 100 nm, respectively, and their aspect ratio was about 12. From Figs.1(a) and (c), it is apparent that the top ends of the tubes are open and the bottom ends of the tubes are closed. The closed bottoms of nanotube indicate the formation of a barrier layer structure similar to that of porous alumina. On the other hand, after anodization in fluoride-free electrolytes no porous structure is observed (Fig.1(d)).

Fig.2 shows current-time curves of Ti recorded during anodization in glycerin+water (70:30 of volume ratio) electrolyte with addition of different amounts of ammonium fluoride at 20 V. In fluoride-containing electrolytes obvious deviations from the curve in fluoride-free electrolyte are observed. The current densities in fluoride-containing electrolytes are higher than those in fluoride-free electrolyte, and increase with increasing the fluoride content in the range of 0-2%. This indicates that the dissolution reaction of the anodic oxide later is induced by F<sup>-</sup> ions. The growth of TiO<sub>2</sub> nanotubes is a result of competition between electrochemical formation oxide and chemical dissolution of oxide by fluoride ions[8]. As can be seen from Fig.2, the formation of TiO<sub>2</sub> nanotube is clearly affected by fluoride in the electrolyte. And a key factor that influences the electrochemistry is the fluoride concentration in the electrolyte. This can be ascribed to additional chemical dissolution of the electrochemically formed oxide layers due to soluble  $[TiF_6]^{2-}$  complexes. In the first step, the current density sharply decreases due to oxide formed on electrolyte/titanium interface with a low conductivity. The current densities start to increase by the actively chemical dissolution reaction due to F<sup>-</sup> ions from electrolyte. The porous structure is formed as a result of the localized chemical dissolution of the oxide by  $[\text{TiF}_6]^{2-}$  according to the reaction (1):

$$TiO_2 + F^- + H^+ \longrightarrow [TiF_6]^{2-} + 2H_2O$$
(1)

$$Ti+H_2O \rightarrow TiO_2+H^++e$$
 (2)

This leads to a higher field at bottom of the pore that drives further oxidation, and field assists dissolution

1 um 400 nn (c) (d) 400 nm 100 nm

Fig.1 FE-SEM images of TiO formed at 20 V for 1 h: (a) Top-view; (b) Cross-sectional; (c) Bottom-view in glycerin+water (70:30 of volume ratio)+1.5% NH<sub>4</sub>F; (d) Top-view in glycerin+water (70:30 of volume ratio) without NH<sub>4</sub>F





**Fig.2** Current densities at 20 V during anodization in glycerin+ water (70:30 of volume ratio) solution with different amounts of  $NH_4F$ 

where Ti ions come out of the metal and dissolve in solution[10]. Finally, the current reaches a steady state. This steady state current increases with increasing fluoride concentration[11].

However, if there is not  $F^-$  ion in electrolyte, the oxide layer is composed of only compact layer instead of nanotubular layer according to the reaction (2). Because acidification from  $[TiF_6]^{2^-}$  is not established at the electrolyte/oxide interface during the anodization, the presence of  $F^-$  ions leads to chemical dissolution of  $TiO_2$  layer and prevents hydroxide precipitation of  $Ti^{4+}$  ions arriving at the electrolyte/oxide interface, so  $Ti^{4+}$  can be complexed to  $[TiF_6]^{2^-}$  before reacting with a hydroxide layer. From the results of XPS measurement, the O 1s spectra (Fig.3) about the chemical state of the  $TiO_2$  nanotubes clearly show that the anodic film consists of oxide (530.1 eV) and a little amount of hydroxide (531.9 eV).

The phases of  $TiO_2$  nanotubes include anatase, rutile and brookite. The structural features of these phases can



**Fig.3** XPS spectra of TiO<sub>2</sub> nanotubes formed at 20 V for 1 h in glycerin+water (70:30 of volume ratio)+1.5% NH<sub>4</sub>F

be explained on the basis of different types of linkages of Ti - O octahedral units[12]. The as-anodized  $TiO_2$ nanotubes are in amorphous structure. Meanwhile, annealed TiO<sub>2</sub> nanotubes are converted to anatase at approximately 280 °C or mixture of anatase and rutile at temperatures higher than 450 °C[13]. From Fig.4(a) it can be seen that, the XRD results of as-anodized titania films show only titanium peaks at  $2\theta$ =52.95° (102), 70.4° (103), and 76.05° (112) that are originated from the Ti substrate. After annealing at 450 °C (Fig.4(b)) for 60 min, anatase phase of TiO<sub>2</sub> nanotubes appears. After annealing at 550 °C (Fig.4(c)), the peaks related to rutile appear, but most of these phases are still composed of anatase. And then rutile phase is dominantly observed more at 650 °C (Fig.4(d)) than that at 550 °C. With the increasing of annealing temperature, rutile peaks become more numerous and strong. The result shows that the various crystal transition of the anatase-rutile phases from amorphous takes place after additional annealing treatment.



**Fig.4** X-ray diffraction patterns of TiO<sub>2</sub> nanotubes after heat treatment at different temperatures for 1 h: (a) As-anodized; (b) 450 °C; (c) 550 °C; (d) 650 °C

#### 4 Conclusions

1) Self-ordered  $\text{TiO}_2$  nanotubes can be formed by anodization for 1 h in glycerin electrolyte with addition of NH<sub>4</sub>F. In fluoride-containing electrolyte, the current densities are higher than those of fluoride-free electrolyte, and increase with increasing the fluoride content in the range of 0–2%. Only compact layer is formed in fluoride-free electrolyte.

2) In fluoride-containing electrolyte, nanotubular layer is formed on Ti substrate. The additional chemical dissolution of the electrochemically formed oxide layers is due to soluble  $[TiF_6]^{2-}$  complexes. Thereby, to achieve self-ordered TiO<sub>2</sub> nanotube, the presence of fluoride in electrolyte is required.

3) The present work shows the chemical

composition between phases of the  $TiO_2$  nanotubes. These indicate that the anodic film is composed of oxide and hydroxide, and the transition of the anatase-rutile phases from amorphous takes place after additional annealing. Clearly, heat treatment has a significant influence on phase transition of  $TiO_2$  nanotubes.

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