Fast growth of self-aligned titania nanotube arrays with excellent transient photoelectric responses

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ABSTRACT

Self-aligned titania nanotube arrays (TNAs) were fabricated by electrochemical anodization at high voltage of 120 V in an electrolyte containing high F^- concentration. Compared to the TNAs obtained by traditional anodic conditions, the resulted samples show more uniform surface, firmer structure, and stronger adhesion to the Ti substrate. Importantly, the anodization time can be greatly reduced from several hours to tens of seconds. The photoelectric current density produced by the new TNAs is 1.94 times higher than that of TNAs prepared under traditional conditions. A new growth mechanism involving columnar oxide etch (COE) model is proposed to explain the inner evolution of the TNAs. The effect of anodic current oscillations on the formation of nanotube, tube ridge, and porous structures are investigated. This ultrafast growth of TNAs will have significant impact on large-scale device applications.

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1. Introduction

Electrochemical anodization technology has received great attentions to produce titania nanotube arrays (TNAs) due to its advantages of low cost, large area fabrication, and highly-ordered and uniform arrays [1–6]. The morphology of prepared TNA is strongly affected by several key factors during anodizing process, e.g. the anodization voltage [7–12], the composition and concentration of electrolyte, [3,13–15] and the anodization time, etc [16]. Previous research has more or less established common parameters for TNAs growth, e.g. anodization voltage less than 80 V [17–21], F^- concentration less than 0.3 M [14,22–24], and anodization time more than 1 h [25–27]. It is not uncommon that a typical deposition of TNAs may take a few hours. In this work, we explored unusual anodization conditions with higher voltage up to 120 V and a higher concentration of F^- up to 0.4 M in electrolyte in order to produce TNAs in very short time. We found that Self-aligned TNAs with firm structure and excellent photoelectric response could be obtained within tens of seconds instead of a few

hours. To the best of our knowledge, there is no report on the anodic TNAs obtained in such short time.

Great efforts have been made to understand the growth mechanism of the porous anodic oxide. Theories introduced to explain the growth process of porous anodic oxide include the field-assisted dissolution (FAD) model, [28–31], the mechanical splitting model, [32] the localized dielectric breakdown model, [33] Ti ion ejection model, [34,35] the viscous flow model, [36–38] and the field-enhanced water dissociation and equifield strength model [39–41]. Each model has its own advantage to give reasonable explanation for TNAs growth up to certain aspects. However, many problems remain to be resolved, such as the gap formation between tubes and the relationship of the current oscillations with the structural evolution during anodization. [40] Houser et al. claimed that no model has successfully explained the relationships between porous anodic oxide morphology and all processing parameters. [42] But it is commonly accepted that the formation of TiO_2 results from the combination of O^{2-} with Ti^{4+} which are ejected from Ti foil under applied voltage and then migrate to the electrolyte/oxide interface. The formation of TNAs is mainly attributed to the anistropic etching of TiO_2 by F^- to form $[TiF6]^{2-}$ complex. [6,42–47]

$$Ti^{4+} + 2O^{2-} \rightarrow TiO_2 \qquad (1)$$

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$$TiO_2 + 6F^- + 4H^+ \rightarrow [TiF6]^{2-} + 2H_2O \qquad (2)$$
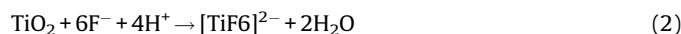
Zhu and coworkers proposed oxygen bubble mould effect (OBME) model and focused on the physical nature of the ionic current and electronic current within the anodic oxide. They pointed out that the ionic current contributed to the formation of the barrier oxide and the electronic current resulted in the oxygen evolution. [48,49] Based on the experimental findings and the OBME model, we propose a new growth model of TNA, i.e. columnar oxide etch (COE) model, which emphasizes the pore generation and the close relationship between the ridge formation and oxygen evolution. [48,49] The problems which could not be solved previously are investigated with this new model, including the origin of the gap formation between the nanotubes, and the interactions between the current oscillations and porous structural features. Moreover, the anodic current density was analyzed in detail in conjunction with the formation of TNAs. This growth model may open new possibilities for understanding the mechanism of TNAs and apply to other oxide nanotube arrays. The well-structured and efficiently produced TNAs with excellent photo-electric response are expected to reduce the production cost and improve the performance of TNAs based devices.

2. Experimental section

2.1. TNA preparation

Titanium foils (0.1 mm in thickness, 99.6% purity) were degreased prior to anodization by sonicating in acetone, rinsing with alcohol and deionized (DI) water subsequently and drying in nitrogen gas. The cleaned Ti foils were then chemically polished in the solution containing HF, HNO_3, and DI water (1:1:5 volume ratio) for 20 s, and then rinsed and dried successively. The electrochemical setup consists of Interlock potentiostat-galvano-stat (IPD-12003SLU) and a classical two-electrode cell with 1.5 cm separation between counter and working electrodes. An area of 1 cm^2 Ti surface was exposed to an electrolyte which contains 0.4 M NH_4F dissolved in a solution of ethylene glycol and DI water (30:1 volume ratio). The anodization of Ti foil was performed at an applied voltage of 120 V without magnetic stir at 10 °C for 4, 20, 40, 60, 80, 120, and 300 s, respectively. The as-prepared samples were rinsed with DI water and then dried by high purity nitrogen gas. The samples were referred to as TNA120 series. In order to compare the structural stability and photoelectric response of TNA120 series with those samples prepared by traditional conditions, another TNA sample was prepared in the electrolyte which contains 0.27 M NH_4F dissolved in a solution of ethylene glycol and DI water (30:1 volume ratio) at 60 V for 3 h. This control sample was referred to as TNA60. All samples were post annealed at 450 °C for 2 h in atmosphere with a heating rate of 5 °C min^{-1}.

2.2. Characterization method

A scanning electron microscope (SEM) Hitachi FE-SEM S4800 was employed for characterizing the structure and morphology of the TiO_2 nanotube arrays. Both top view and cross section of the TNAs were measured. The photoelectric response of the samples anodized at 120 V for different time and 60 V for 3 h was recorded with an electrochemical workstation (CHI660E) in a standard three-electrode configuration with a platinum plate as the counter electrode, SCE as the reference electrode, and the sample as the working electrode. The support electrolyte was 0.5 mol L^{-1} Na_2SO_3 aqueous solution. A white light source was utilized as an excitation source (intensity: 150 mW cm^{-2}).

3. Results and Discussion

3.1. Morphology

The morphology of TNA120 series and TNA60 were measured by SEM and are shown in Fig. 1. It can be seen that the pores started to form as early as 4 s [Fig. 1 (a)]. The top view clearly shows the nano-pores of about 50 nm were formed. Due to the very short time, the pores are very shallow as shown in the inset of Fig. 1(a). The depth of the pores is about 50 nm also. Therefore no tubular structure was observed at this stage. The pores are uniformly distributed on an initial oxide layer with about 50 nm thickness. This uniform porous structure may be practically useful for loading other nanomaterials. As the anodization time was increased up to 20 s, one can see that clear tubular structures were obtained and the tube length increases with the anodization time. The average pore diameter shows a slight and continuous increase till 80 s as shown in Fig. 1 (e). Some tube mouths also start to be separated from their neighboring tubes. After the growth of 80 s, most tube mouths are uniformly distributed and become independent from each other with narrow distance between them. The average tube length has reached 3.5 um after 80 s. As the anodic time continued to increase to 120 s, the tube mouths are found to be broken and the surface becomes rougher than that of those anodized for short time. The tube length increases to about 5 um. Further increase in growth time up to 300 s results in a more broken of the tube mouths but does not cause a significant change in tube length. This observation may suggest that the growth of the TNAs at the bottom is compensated by etching at the tube mouth. Fig. 1 (h) shows the surface and cross sectional images of sample TNA60. One can see that the diameter of tubes is about 100 nm which is larger than those grown at 120 V and the gap between the nanotubes also increases. It is mainly because the anodization duration under 60 V is 3 h, allowing long time of chemical dissolution of the tube walls. Two or more adjacent tubes would be reconstructed to one tube, resulting in the larger tube diameter and space between the tubes.

The quantitative morphology parameters are listed in Table 1, including diameter and tube length. From Table 1, it can be seen that the pore size increases slightly with anodic time but keeps steady from 80 s while the whole film thickness (tube length) increases continuously from 4 to 300 s.

Fig. 2 displays the tube length as a function of anodization time. From 4 to 60 s, the tube length grows linearly with anodization time but the growth rate slows down gradually after 60 s. High anodic voltage is beneficial to the field-assistant dissolution as described by Eq. (1), leading to the fast formation of TiO_2 barrier layer on Ti foil. It is the base for the growth of TiO_2 nanotube arrays. The F^- is contributed to the chemical dissolution of TiO_2 as described by Eq. (2), which is responsible for the tubular structure formation. However, the high voltage and high concentration of F^- has a double-edge effect on the nanotube growth. In the beginning of the anodization duration, it is essential for the fast growth rate of the TiO_2 nanotube arrays. As the TiO_2 nanotube arrays grow, more and more potential is dropped on the TiO_2 nanotube arrays, resulting in the less formation speed of TiO_2 barrier layer. But the chemical dissolution is high on the top region of the TiO_2 nanotube arrays due to the high F^- concentration and mobility, leading to the lowered growth speed of the TiO_2 nanotube arrays and even the damage to the tube mouth. In this case, as the anodization time reaches 60 s, on one hand, lengthened nanotube arrays reduce the formation speed of TiO_2 barrier layer; on the other hand, the dissolution of the initial oxide layer allows more F^- to attack the tube mouths, leading to the lowered growth speed of nanotube arrays after 60 s. The insets show the optical photographs of the samples anodized for 20, 80, and 120 s, respectively. The TNA120 sample of 20 s displays a colorful fringe pattern which is due to the