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Formation and mechanistic study of self-ordered TiO_2 nanotubes on Ti substrate

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Abstract

The formation of anatase TiO_2 nanotubes by anodic oxidation on a pure titanium substrate in an aqueous solution containing 0.5 wt.% NaF was investigated. Nanotubes with a length of 3 μm in a nanotubular TiO_2 film were obtained in the pH 4.2 electrolyte. In strong acidic solution (pH 1.5), TiO_2 nanotubes of short length were formed due to the fast chemical dissolution rate. In this case, there was no variation of the average pore diameter and wall thickness of the TiO_2 nanotubes. From this experiment, it was again confirmed that the pH value of the electrolyte controls the thickness of the well-aligned TiO_2 nanotubes. A mechanistic study of the formation of the TiO_2 nanotubes was performed based on the observation of the surface morphology (top-view and cross-sectional view) using FE-SEM and the analysis of the current density–time curves. Furthermore, the morphology of the anodized TiO_2 film shows a rough surface and irregular wall thickness, since the anodic reaction was performed in an aqueous solution containing F^- ions. The origin of this morphology was dealt with in detail in the FE-SEM study. The crystal structure of the TiO_2 nanotubes was confirmed using XRD and Raman analyses.

Keywords: Anodic oxidation; Titanium oxide; Nanoporous structure; Nanotube; NaF electrolyte

1. Introduction

In the past few years, high surface area and nanoporous TiO_2 nanotubes have attracted much attention for their potential use in several practical applications requiring an interconnected and large internal surface area, such as photoelectrochemical solar cells [1–3], electrochromic windows [4,5], photocatalyts [6], sensors [7], and Li ion batteries [8]. More recently, titania nanotubes with different sizes and various geometrical shapes were prepared using various physical and chemical synthesis routes such as sol–gel [9], template synthesis [10,11], hydrothermal process [12–14], and anodization [15]. As an effective fabrication technology, the electrochemical anodization process is useful because of its low cost, large area fabrication, good mechanical adhesion, and electrical conductivity due to the nanotubes being directly connected to the substrate, while the limited thickness of these anodic TiO_2 nanotubes must be adjusted by controlling the anodic conditions, such as the applied voltage, electrolyte composition, the pH of the electrolyte, duration, and magnetic agitation [16,17]. Especially, the composition of the electrolyte is an important factor during anodization.

In earlier research work, titanium oxide with a nanotubular and porous structure was fabricated via anodic oxidation in an acidic HF-based electrolyte [18], while, typically, the porous TiO_2 layers were grown 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 layer rather than the formation of a titanium oxide layer by the chemical oxidation process, hindering the thickening of the porous layer. Herein, we studied a variety of electrolytes in an attempt to grow longer TiO_2 nanotubes, viz. H_2SO_4/HF-based [19], $NaHSO_4$/KF-based [20], NaF/Na_2SO_4-based [21], and organic-based electrolytes [22]. Recently, the Patrick group reported on the formation of anodic TiO_2 nanotubes in neutral $(NH_4)_2SO_4/NH_4F$ aqueous solution [23]. In this study, self-ordered TiO_2 nanotubes with a high-aspect ratio and a length of 2.5 μm were formed in a neutral aqueous solution of NH_4F and $(NH_4)_2SO_4$. The authors suggested that controlling the pH at both the tip and bottom layer of the tubes is important to grow longer TiO_2 nanotubes.

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However, some irregularity in the pore formation process and an uncertain formation mechanism were reported.

Herein, we obtained high-aspect ratio and self-organized porous TiO_2 nanotubes (3 μm) and conducted a formation and mechanistic study in a NaF-based electrolyte using a DC power supply as an applied power source.

2. Experimental

Titanium sheet (99.9% purity, Nikko Metal, Japan) with a thickness of 0.5 mm was cleaned by sonicating it successively in acetone, ethanol, and deionized water (DI), for 10 min each, followed by drying in an air stream. A specimen of the Ti sheet with a size of 1.5 cm × 2 cm was cut and copper wire was attached to the upper front side of this specimen using conductive epoxy adhesive. Then, after drying, all areas, except for the actual exposure area of 1 cm^2 on the front side, were pasted using nonconductive epoxy adhesive on both sides and dried in the oven. For the electrochemical anodization of the Ti sheet, we used a DC power supply (ODA technologies, 0∼120 V) connected to a multimeter interfaced to a controlling computer. Constant voltage anodization was carried out using a two-electrode configuration with a working electrode made of Ti sheet and a counter electrode made of Pt wire. All experiments were conducted at room temperature, viz. 23 °C, and an applied voltage of 20 V. The distance between the anode and cathode was kept at about 3 cm. Various experiments were conducted, in which the anodizing time was varied for the mechanistic study. As the electrolyte for the electrochemical anodic reaction, we used a mixture of 0.5 M Na_2SO_4, 0.5 M H_3PO_4, 0.2 M sodium citrate, and 0.5 wt.% NaF solution and the pH was adjusted to between 1.5 and 5 by adding NaOH reagent. The electrolyte was stirred continuously at 150 rpm using a magnetic stirrer. The anodized samples with a porous structure were washed and sonicated in DI water for 5 min to remove the remnants on the surface and then blown dry in an air stream. In order to improve the crystalline properties and remove the remnants or barrier oxide layer after the anodic reaction, the as-anodized samples were annealed at 500 °C for 2 h under air ambient.

The thickness and morphology of the anodic TiO_2 nanotubes were confirmed by means of a JSM-6330F field emission scanning electron microscope (FE-SEM, JEOL, Inc.) operating at 10 kV. The surface composition of the samples was analyzed using energy dispersive spectroscopy (EDS). The crystalline phase and structure were analyzed using high-power X-ray diffraction (Rigaku D/MAX 2500 V diffractor) with Cu K_α radiation at 40 kV and 100 mA. Raman spectroscopy was conducted at room temperature using a Jobin Yvon Model (LabRam HR) Raman spectrometer from France equipped with a CCD detector. The 632 nm radiation from a He–Ne laser was used as the excitation source.

3. Results and discussion

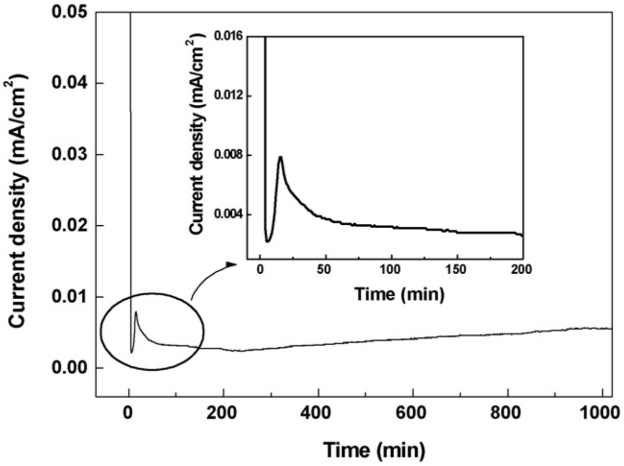

Fig. 1. Current–time response at a constant voltage of 20 V in the pH 4.2 electrolyte. The sample anodized for 18 h, with the inset showing the magnified view in the initial stages of anodizing time.

Fig. 1 shows the current density as a function of the anodization time in intervals of 60 s. In the initial step of anodization (up to 30 s), an abrupt decrease of current was observed, due to the formation of a barrier layer which induces a voltage drop between the working electrode (Ti sheet) and electrolyte [24]. In the second step (from 30 to 45 s), a sudden increase of current was observed due to the active chemical dissolution reaction of the suddenly formed oxide layer induced by F^- ions from the electrolyte, leading to the formation of a porous structure. In the third step (after 45 s), a relatively constant equilibrium state was maintained with increasing the anodizing time, while the current density slightly increased, showing an oscillation curve. The previously reported reaction scheme includes an abrupt decrease of current in the initial stage of anodization, followed by a gradual increase of the current density and then a decrease of the current density up to the final stage [25]. However, in the present experiment, the anodic current during anodization kept increasing slowly, while the anodic reaction was maintained at the equilibrium state between the chemical dissolution process and chemical oxidation process. This result may be attributed to the remnant of the anodic reaction, $[(TiF_6)^{2-}]$, and the decrease in the length of the barrier layers. Moreover, the anodic current in the overall reaction steadily increased. The related mechanistic process for the formation of self-ordered titanium oxide has been previously reported [26].

$$Ti + 2H_2O \rightarrow TiO_2 + 4H^+ (\text{hydrolysis of titanium}) \tag{1}$$

$$TiO_2 + 6HF \rightarrow [TiF_6]^{2-} + 2H_2O + 2H^+ \quad (\text{dissolution of } TiO_2 \text{ to form the pores}) \tag{2}$$

The above two reactions proceed alternatively in the overall reaction. The hydrolysis of Ti and the dissolution of TiO_2 lead to an increase in the pH value due to the large quantity of H^+ ions that are released. The variation of the pH value is about 0.05 in the pH 4.2 electrolyte and about 0.08 in the pH 4.8 electrolyte (not shown here). After 1 min of anodization, the pH value oscillated in the range of ±0.03. This means that proton