The rapid growth of 3 μm long titania nanotubes by anodization of titanium in a neutral electrochemical bath

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Abstract

The length of titania nanotubes formed by anodization of 0.1 mm thick titanium foil was found to be a strong function of the pH of the electrolyte. The longest nanotubes were formed by using an electrolyte consisting of 1 M Na_2SO_4 plus 5 wt% NH_4F with pH 7. At this pH, after 30 min of anodization, 3 μm length nanotubular titania arrays with top diameters of ~ 50 nm and bottom diameters of 100 nm were produced. No acid was added to this electrolyte. The formation of titania nanotubes in neutral pH systems was therefore successful due to the excess NH_4F in the electrolyte which increases the chemical dissolution process at the metal/oxide interface. Since the pH of the electrolyte at the top part of the nanotubes is kept very high, the dissolution of the nanotubes at the surface is minimal. However, the amount is adequate to remove the initial barrier layer, forming a rather well-defined nanoporous structure. All anodized foils were weakly crystalline and the transformation to anatase phase was achieved by heat treatment at temperatures from 200 to 500 °C for 1 h in air. Annealing at temperatures above 500 °C induce rutile phase formation and annealing at higher temperatures accelerates the diffusion of Ti^{4+} leading to excessive growth and the nanotubular structure diminishes.

1. Introduction

Titanium dioxide, titania, has been investigated extensively in recent years because of its outstanding catalytic and optoelectronic properties for example in photocatalysis for the purification of polluted air and water [1–5], as photoelectrical cells for water splitting [6, 7] and as photoanode in dye sensitized solar cell [8–11]. For these applications nanostructured titania is the most preferred as it has larger surface area. Also, the anatase form of titania is preferential over rutile and brookite. Anatase is metastable but can be formed when amorphous titania is heat treated [12]. Anatase titania has higher electron mobility by an order of magnitude

compared to rutile and in terms of its crystal structure, the specific surface area of anatase is higher compared to rutile which is important for energy conversion devices as well as in the enhancement of photocatalytic property of the oxide [3].

The nanotubular structure is of great interest due to their high surface-to-volume ratio. The electrochemical formation of nanotubular titania has attracted much attention recently [13–18] and most works have reported on the formation of the nanotubes in acidic electrolyte. Recently, we have reported on the formation of the self-organized structure, illustrated in figure 1 by anodization in an electrolyte with pH ~ 7 in electrochemical bath with 3 wt% NH_4F [17]. In this present work, the effect of pH on the morphology and dimension of the nanotubes was further studied in a bath with 5 wt% NH_4F . The aim is to produce relatively

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Figure 1. Schematic illustration of TiO₂ nanotubular structure.
(This figure is in colour only in the electronic version)

long nanotubes at as short anodization times as possible. Unlike other works reported on the subject, it was found that 3 μm long nanotubes were successfully formed after 30 min of anodization in bath with excess NH_4F but without any addition of acid. Such a simple and rapid formation would be of interest for large scale production of the nanotubes. Nonetheless, the anodized titanium foils were amorphous and would require heat treatment for phase formation. The effect of heat treatment on the nanotubular structure was studied to explore the temperature at which anatase titania would form and to investigate the robustness of the nanotubular structure when subjected to heat treatment process.

2. Experiment

High purity titanium foils with thickness of 0.1 mm (99.96% purity, Advent Research Materials, England) were subjected to potentiostatic anodization in a two-electrode electrochemical cell at room temperature. Prior to anodization, the foils were cut into 1 cm $\times$ 2 cm, and were cleaned with ethanol and sonically cleaned in iso-propanol for 15 min. After drying, the foil was immersed in 1 M Na_2SO_4 electrolyte consisting of 5 wt% NH_4F . The pH of the solution was measured using Hanna Instrument pH meter. Without any acid addition, the pH recorded was ~ 7 and the pH was varied by the addition of H_2SO_4 to the electrolyte. Anodization was carried out for 30 min at constant voltage of 20 V with sweep rate of 0.1 V s^{-1} . To view the surface profile of the samples, field emission scanning electron microscope (FE-SEM) Zeiss Supra 35 was employed utilizing in-lens mode to view the morphologies better. In order to determine the thickness of the anodic film produced, a cross sectional morphology of the sample was viewed under FE-SEM placed on a 45° tilt angle sample stage. The morphological characterization used. Anodized titanium was then subjected to heat treatment process at 300–800 °C in air for 1 h. The sample was placed in an alumina boat and the furnace was heated at the rate of 10 °C min^{-1} and cooled. X-ray diffraction analysis was

conducted on the samples before and after annealing using XRD Philip model PW 1729. Raman spectra analysis was conducted by using Raman spectroscopy model Jobin Yvon HR 8-UV.

3. Results and discussion

3.1. Morphologies

Figure 2(a) is the FE-SEM image titanium foil before anodization. As seen, under high magnification, the surface consists of possibly a thin layer of air formed oxide. After anodization, the morphologies change significantly as seen in figures 2(b)–(d) for samples anodized at 20 V in electrolyte with pH of 2, 4 and 5 respectively. As seen in these images, after 30 min of anodization, self-aligned nanotube arrays are successfully formed. The area of nanotubes coverage is excellent as well. It could also be seen that the length of the nanotubes increases from ~ 300 nm to 1.3 μm as the pH of the electrolyte was increased from 2 to 5. Insets in figures 2(b)–(d) are the surface morphologies of the anodized foils. For samples made in electrolytes with pH 2 and 4, the diameter of the nanotubes is uniform throughout the length of the tubes (~ 100 nm) but for sample anodized in electrolyte with pH 5, the diameter at the top of the nanotubes is smaller with average diameter of 70 nm. Anodization performed in electrolyte with pH 7 resulted in 3 μm long nanotubes as seen in figure 3(a). In figure 3(b), a large area of uniform porous structure was observed indicating the success in the formation of the nanotubular structure at a short anodization time of 30 min in neutral electrolyte. Similar to the sample anodized in electrolyte with pH 5, the diameter of the nanotube at the surface is much smaller (50 nm) than at the bottom (100 nm). Figure 3(c) shows the bottom part of the nanotube. As seen in the figure, the bottom part is conical in shape and is closed.

Key to achieving the control over the length of the nanotubular structure is an adjustment of the electrolyte composition and its pH. During the formation of the nanotubular structure, three main initial processes occur: (1) the formation of the thin anodic oxide (passivation layer), (2) electric field dissolution of the thin passivation layer forming pits and (3) attack of these pits by the fluoride ions to form a porous structure. Only selective pores will survive promoting the self-organized nanotubular structure. Passivation equation can be expressed as in (1).

When this happens, a large amount of H^+ ions are produced. Distribution of H^+ ions inside the nanotubes is shown schematically in figure 4. The existence of H^+ as well as excess F^- ions in the solution will induce the chemical dissolution process. Such a process is shown in equation (2).

Inside each nanotube, the chemical dissolution process will continue to happen at the metal/oxide interface. As the chemical dissolution removes the oxide in this region

Figure 2. FE-SEM image of the titanium foil (a) before anodization and after anodization in electrolyte with pH, (b) 2, (c) 4 and (d) 5. Insets in ((b)–(d)) are the surface morphologies of the nanotubes.

Figure 3. SEM morphology of titania made in electrolyte with 5 wt% NH_4F , pH = 7, (a) cross sectional, (b) surface and (c) the bottom part of the nanotubes.

i.e. at bottom part of the nanotube, anodic oxidation occurs again. This will induce the formation of nanotubes with a closed bottom as observed in figure 3(c). As the anodic oxidation continues, more H^+ will be produced at the metal/oxide interface. The excess H^+ inside the nanotube will generates local acidification. This will accelerates the chemical dissolution rate (equation (2)), lengthening the nanotubes even further. However, chemical dissolution also occurs at the top part of the nanotubes at the oxide/electrolyte interface limiting the length of the nanotubes.

The influence of the pH of the electrolyte on the structure of the anodized titanium observed in this work can be understood by considering the local acidification inside the nanotube as well as chemical dissolution process which occur at the top part of the nanotubes.

To induce a growth of long nanotubes at as short anodization time as possible, the pH gradient must be controlled so that the local acidification inside the nanotubes along with the fluoride ions would accelerate the inwards growth. The chemical dissolution at the top part must however

Figure 4. Schematic diagram of the growth of nanotubes at pH = 7. $H^+ \downarrow$ indicates less H^+ ions and $H^+ \uparrow$ indicates excess H^+ ions.

Figure 5. Raman spectra for as-anodized sample and samples annealed at different temperatures from 300 to 700 °C in air for 1 h (samples were prepared by anodization in bath with pH = 7).

be significantly reduced. In this work, the use of excess NH_4F was found to be beneficial in promoting the inward growth of the nanotubes while the content of H^+ at the top of the nanotubes (oxide/electrolyte) interface is reduced (Figure 4). In Figure 3(a), it is observed that there exists a diameter gradient along the length of the nanotubes with larger nanotubes diameter at the metal/oxide interface. Such variation can be also explained by the local acidification which occurs laterally as well as inwards increasing the diameter of the nanotube at this region. Such variation is illustrated in Figure 4.

As indicated in Figure 4, if the nanotubes are made in acidic electrolyte, the top part of the nanotubes is subjected to continuous chemical dissolution. As the chemical dissolution occurring in this region occurs uniformly, a well-defined ring-like structure is observable under the SEM and the diameter of the nanotubes appears to be consistent across the tube length. However, in conjunction to this, shorter tubes results since etching will remove a considerable part of the nanotubes. This is observed for samples made in electrolyte with pH 2 and 4 (Figures 2(a) and (b)). For samples made at pH 5 (Figures 2(c)) and 7 (Figure 3), it is inferred that since the electrolyte does

Figure 6. X-ray diffraction patterns for annealed nanotubes made in electrolyte with pH = 7 (annealing at 300–700 °C for an hour in air).

not have adequate H^+ , less chemical etching occurs at the surface. The resulting nanotubes structure is therefore not as clearly defined as those made in electrolyte with pH 2 and 4 but the length of the nanotubes is rather long. Therefore, the control over the length of the nanotubes can be achieved by suppressing the chemical dissolution at the top part of the nanotubes whilst promoting the local acidification inside the nanotube at the metal/oxide interface. Another interesting feature of the nanotubes is the serration at the nanotube walls as seen clearly from the cross section of the oxide in Figures 3(a) and (c). The existence of such structure is due to current oscillation during the anodization process which induces ridges at the nanotube walls [13].

3.2. Structural analyses

Nanotubes formed by anodization in fluorine-contained electrolyte are amorphous and heat treatment is necessary for the formation of desired titania phase. Raman spectroscopy measurements were carried out on the anodized titanium before and after heat treatment at 200–700 °C for an hour in air (Figure 5). There are two extremely broad Raman bands for the as-anodized titanium at 130–280 and 590–670 cm^{-1} . Although the framework structure is indeed amorphous the existence of these broad Raman shifts are characteristic of anatase titania. This could indicate partial crystallinity of the anodized foils. For a single crystal anatase titania, Oshaka *et al* [19] reported on the detection of six Raman active modes: $A_{1g} + 2B_{1g} + 3E_g$. The corresponding Raman allowed bands are 144 cm^{-1} (E_g), 197 cm^{-1} (E_g), 399 cm^{-1} (B_{1g}), 513 cm^{-1} (A_{1g}), 519 cm^{-1} (B_{1g}) and 639 cm^{-1} (E_g). On the other hand, rutile has four Raman active modes: $A_{1g} + B_{1g} + B_{2g} + E_g$ detected at 143 cm^{-1} (B_{1g}), 447 cm^{-1} (E_g), 612 cm^{-1} (A_{1g}) and 826 cm^{-1} (B_{2g}).

The Raman spectrum for sample annealed at 300 °C is made up of four main characteristic bands at 147.1, 400.1, 518.3 and 637.5 cm^{-1} , all of which are characteristic peaks of anatase titania. A less prominent peak can be seen at ~ 200 cm^{-1} which is also associated anatase titania. As the annealing temperature was increased to 400 °C, Raman intensity becomes stronger which may indicate the growth of the anatase crystals within the titania nanotubes walls.

Figure 7. FE-SEM images of heat treated samples at (a) 300 °C, (b) 500 °C, (c) 600 °C and (d) 800 °C (in air, for an hour). Cross sectional images are for sample heat treated at (e) 500 °C, (f) 600 °C (air, for an hour).

The position of the E_g band centred at 144 cm^{-1} has now shifted to a lower value supporting the argument that more anatase crystallites are present in the nanotubes. At 500 and 550 °C, the intensities of the spectra reduce. The reduction of the intensities could be attributed to the onset of anatase to rutile phase transformation. However as the nanotube wall is very small ($\sim 10\text{ nm}$) the possibility of the reorientation of the Ti-O bond to form stable rutile phase may have been inhibited significantly forming extremely small rutile crystallite to be detected. This inhibition effect has also been reported for nanoparticles with size less than 10 nm and also for mesoporous titania. Such inhibition is often been attributed to the interference of the rearrangement of the chemical bonds in the crystallites leading to the stabilization of anatase titania. When the annealing temperature was increased to 600 °C, the formation of rutile titania is evident from the characteristic Raman shifts at 144, 452 and 612 cm^{-1} . Vibration mode at $\sim 800\text{ cm}^{-1}$ is barely detectable but a peak centred at 250 cm^{-1} can be detected which according to Qian *et al* [20] could be attributed to a Ti-OH bond. For this sample, Raman shifts associated to anatase titania can also be detected but at a much lower intensity. The intensity associated with rutile phase becomes more intense for sample annealed at 700 °C. At 700 °C (and above), the detection of rutile is possible not only due to the phase transformation but also because of excessive grains growth, leading to sintering of the nanotubes due to oxidation.

X-ray diffraction patterns of annealed nanotubes are shown in figure 6. Anatase titania could not be detected

for sample annealed at 300 °C but a peak associated to (101) anatase at 25.5° is seen for sample annealed at 400 and 500 °C. Samples annealed at 600 °C has diffraction patterns of both anatase and rutile titania ((110) rutile peak at 27.5°). Only rutile diffraction patterns can be detected for sample annealed at 700 °C.

Surface morphologies of annealed nanotubes at 300 °C, 500 °C, 600 °C and 800 °C are shown in figures 7(a), (b), (c) and (d) respectively. Indeed the surface morphologies of the nanotubes change as a function of the annealing temperatures. From this work, it is evident that growth along the nanotube walls occur and hence the nanotubular can only be retained at annealing temperature $< 500^\circ\text{C}$. At even higher temperatures, the inward O^{2-} diffusion and diffusion of Ti^{4+} from the underlying substrate occurs at an accelerated rate along the nanotube walls leading to excessive growth. This result in the thickening of the nanotubes wall from $\sim 10\text{ nm}$ for the as-anodized sample to 40 nm and 60 nm for samples heat treated at 500 and 600 °C respectively (figures 7(b) and (c)). Agreeing with the structural analyses, as the thickness of the nanotubes walls increase, more rutile titania can be detected in both Raman spectra and x-ray diffraction patterns. Therefore the possibility of the formation of rutile is only possible when the nanotube walls are grown to a certain thickness whereby the Ti-O bond in anatase can now have enough area for rearrangement to form the rutile titania [12]. Figures 7(e) and (f) are the cross sectional morphologies of nanotubes after being annealed at 500 and 600 °C. As the temperature of annealing was increased, the oxidation at the barrier layer

accelerates, shortening the nanotubes. The new crystals which grow as a result of oxidation at the barrier layer of the nanotubes (oxide/metal interface) are mostly rutile. As the annealing temperature is increased to 800 °C, the crystal grows further at the expense of the nanotubular structure. At this temperature, protrusion emanate from the underlying titanium substrate destroying the nanotubular structure completely [21].

4. Conclusion

Large area, self-organized nanotubular titania arrays with top diameter of 50 nm and bottom diameter of 100 nm were formed by anodization of titanium foil in 1 M Na₂SO₄ added to it 5 wt% NH₄F. The solution pH was ~7. The formation of nanotubes with length reaching 3 μm after 30 min of anodization indicates fast rate of nanotubes formation under this anodization condition. The transformation from weakly crystalline titania to anatase phase was performed at 400 °C for 1 h in air. At this temperature, Raman spectroscopy analysis revealed four Raman shifts belonging exclusively to the anatase phase. At 600 °C, rutile titania can be observed. The corresponding morphology of the nanotubes changes with annealing temperatures. Excessive diffusion of Ti⁴⁺ along the nanotube walls induces grain growth hence thickening the walls. The diffusion of Ti⁴⁺ and inwards diffusion of O²⁻ at the oxide/metal interface lead to the oxidation at the metal/oxide interface shortening the nanotubes. Annealing at 700 °C, accelerates the diffusion of Ti⁴⁺ leading to excessive grain growth and the annihilation of the nanotubular structure altogether.

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