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Titanium oxide nanotubes anodized in aqueous and non-aqueous electrolytes

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Titanium oxide nanotubes having a very large surface area are very attractive for battery, gas sensor, photo catalytic applications, and as biomaterials. Titanium of 99.7% purity was anodized in 1 M potassium phosphate monobasic (KH_2PO_4) water solution, glycerine, and ethylene glycol with 0.15 M, 0.17 M, and 0.075 M NH₄F. Titanium oxide nanotubes were fabricated at an anodization maximum potential of 25 V in the aqueous solution, 50 V in glycerine, and 60 V in the ethylene glycol solution. The maximum lengths of nanotubes were 3.0 µm, 14 µm, and 164 µm, respectively. The diameter and length of the titanium oxide nanotubes were compared. The diameters of nanotubes were from 100 nm to 150 nm in the aqueous and ethylene glycol solutions but on the other hand the diameter was 60 nm in glycerine. These differences come from the properties of the anodization solution such as the viscosity and ionic strength of the solutions (electric conductance) and these are key factors for titanium anodization. After anodization, annealing at 500 °C for 30 minutes was followed and the anatase phase appeared on the surface of the titanium nanotube. From electron-diffraction patterns obtained by the fast Fourier transform (FFT) of HRTEM images, the measured angle between the (011) and (101) planes was 82.2°, which was consistent with the theoretical value of the anatase structure. From results of this study, we could control the morphology of titanium oxide nanotube arrays by anodization.

Key words: TiO₂ nanotubes, Morphology, Aqueous, Glycerine, Ethylene glycol.

Introduction

The surface of "valve metals" (Al, Ti, Ta, Nb, V, etc.) are instantaneously covered with a native passivation oxide layer when these metals are exposed to an oxygencontaining environment [1, 2]. The passivation oxide layer gives excellent resistance even to various acid solutions. Creating a passivation oxide layer is good property for nanotube arrays so we dissolved the oxide layer of valve metals with fluoride ions in some solutions by an anodization method. Titanium oxide is a promising material because of its biocompatibility, self-cleaning ability, gas-sensing capability, photo-electrochemical conversion capacity, and photo-catalytic ability.

Over decades many porous materials made by anodizing have been reported in particular anodic aluminum oxide (AAO) [3-8]. Recently, we have reported the mechanism and parameters controlling the formation in fluoridecontaining electrolytes [9]. From these results, the applied voltage is the driving force for anodization but a high voltage leads to micro discharges and a sponge form oxide layer in an aqueous electrolyte. The fabrication of self-aligned valve metal oxide nanotubes have been attracting considerable fundamental and technological interest because of the important applications in sensing, separation, electronics, optoelectronics, and as biomaterials [10-12]. In this study, we report the forming method of TiO₂ nanotubes in different solutions such as an aqueous solution, glycerine, and ethylene glycol. The morphologies of TiO₂ nanotubes made with different solutions were compared and the crystal structure was analyzed. We suggest it is possible to control the morphology of TiO₂ nanotubes.

Experimental

Titanium foil of 2 mm thickness with a large surface area 20 × 20 mm (99.7% purity, Aldrich Chemical Company Inc., Milwaukee, U.S.A.) was used as the anodes. We polished the titanium electrode with SiC 4-6 µm grit (#2000) and cleaned with acetone, isopropanol (2-Propanol), methanol and de-ionized water with ultra sonication to degrease the surfaces prior to the experiments. The counter electrode was tantalum foil 0.25 mm thick and 50×50 mm (99.9% purity, Aldrich Chemical Company Inc., Milwaukee, U.S.A.). Metal electric wires were attached to the two electrodes and sealed by polyester to separate them from the acid electrolyte. The anodization experiments were conducted at a constant potential with a DC power supply (E3643A, Agilent Technologies, Inc.). The time variable current was monitored using a digital multimeter (Model 34401A, Agilent Technologies, Inc.) interfaced with a computer. The temperature of the electrolyte was controlled

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Fig. 1. Top-view SEM images of the titanium oxide nanotube arrays; (a) in aqueous solution, (b) in glycerine, and (c) in ethylene glycol.



Fig. 2. Profile SEM image of the titanium oxide nanotube arrays; (a) in aqueous solution, (b) in glycerine, and (c) in ethylene glycol.

in a water bath and the pH was measured with a pH meter (Model PH211, Hanna Instruments, U.S.A.). For the surface morphological assessment and the length analysis of titanium oxide nanotubes, top view, profile, and bottom view scanning electron microscope (SEM; Model FE-SEM S-4700, Hitachi) observations were carried out. Characterization of the materials produced was made by X-ray diffractometry (XRD, Rigaku D/MAX-RC) using Cu K α radiation. Characterization of the anodic growth titania nanotubes was made by transmission electron microscopy (TEM) (Philips CM 200), fast Fourier transform (FFT) and selected-area electron diffraction (SAED).

Results and Discussion

To control the morphologies of the titanium oxide nanotubes array, we have studied the mechanism of TiO_2 anodization by changing the solution. Fig. 1 shows top-view SEM images of the titanium oxide nanotube arrays; (a) in aqueous solution, (b) in glycerine, and (c) in ethylene glycol, respectively. There were some differences among the morphologies of the nanotube arrays. In the aqueous solution and ethylene glycol, the outer diameter of the nanotubes was about 110-130 nm but in glycerine it was 60 nm. These differences arise from the conductivity and viscosity of the anodization solutions. The diameter of the nanotube anodized in glycerine was narrow. This was due to the high viscosity of glycerine and low mobility of the fluoride ions.

Figure 2 shows profile SEM images of the titanium oxide nanotube arrays; (a) in aqueous solution, (b) in glycerine, and (c) in ethylene glycol, respectively. In these aqueous solutions, the lengths of nanotubes are 3 μ m, 14 μ m, and 164 μ m, respectively. A high conductivity or ionic strength of the anodizing solution is needed to make TiO₂ nanotubes long, but too high a conductivity causes micro-arcs, and

namely, electrical breakdown. A high electrical conductivity of the solution makes the nanotube short by a micro-arc. In aqueous solutions, their high electrical conductivities give a limit in length. In the case of glycerine, having a low electrical conductivity make it a good candidate electrolyte, but its high viscosity cannot make long TiO_2 nanotubes. The fluoride ions could not be attracted to the anode after the nanotube length grows above a limit. This is the reason that glycerine is not a good electrolyte for growing long TiO_2 nanotubes. The longest TiO_2 nanotubes were obtained in ethylene glycol because it had a lower viscosity than glycerine.

Figure 3 shows X-ray diffraction patterns excited with Cu K α radiation. TiO₂ nanotubes from all of the electrolytes were changed to the anatase structure after annealing at



Fig. 3. X-ray diffraction patterns using Cu K α radiation showing the anatase structure after annealing at 500 °C for 30 minutes; (a) annealed at 500 °C for 30 minutes, (b) as-anodized, (c) Ti plate.

Titanium oxide nanotubes anodized in aqueous and non-aqueous electrolytes



Fig. 4. Microstucture of annealed titanium oxide nanotube; (a) bright-field TEM image, corresponding SAED pattern in inset, (b) HRTEM image of a fractured part, FFT electron-diffraction pattern of the region A in inset.

500 °C for 30 minutes. The microstructure of the TiO_2 nanotube was also investigated by high-resolution transmission electron microscopy (HRTEM). Figure 4 shows micrographs of individual titania nanotube. A brightfield TEM image showed that the outer diameter of the nanotube and tube wall thickness, as shown in Fig. 4(a), were 100 nm and approximately 20 nm, respectively. The electron diffraction pattern inset in Fig. 4(a) has several continuous rings which indicates that the nanotube was composed of randomly oriented TiO₂ crystallites. A few large crystallites diffracted more strongly and make the ring pattern "spotty". In some cases, a tube consisted of very large crystallites. Figure 4(b) shows a HRTEM image of such a can. The lattice image was clearly observed, indicating a high crystallinity. Crystal fringes can be seen that have a separation of 3.51 Å corresponding to the spacing of the (101) lattice planes of the anatase TiO_2 structure. Inset in Fig. 4(b) shows the electron-diffraction pattern obtained by the fast Fourier transform (FFT) of this region. The electron diffraction spots were indexed based on the anatase structure. The angle measured between the (011) and (101) planes of 82.2°, as compared to the theoretical value of 82.15°, was consistent with the anatase structure.

Conclusions

We suggest that it is possible to control the morphology of TiO_2 nanotubes by suitable choice of an electrolyte. The key factors are the viscosity of the electrolyte and electrical conductivity of the electrolyte. To obtain the long TiO_2 nanotubes, an electrolyte with low viscosity and a low electrical conductivity should be chosen. TiO_2 nanotubes from all of the electrolytes changed to the anatase structure after annealing at 500 °C for 30 minutes. From an electrondiffraction pattern obtained by the fast Fourier transform (FFT) of HRTEM, the angle measured between the (011) and (101) planes was 82.2°, which was consistent with the theoretical value for the anatase structure.

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