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Anatase type titania nanotube arrays direct fabricated by anodization without annealing

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ABSTRACT

In this paper, anatase type titania nanotube arrays were direct fabricated by anodization in dimethyl sulfoxide electrolyte containing 1 wt% HF solution at above 50 °C without subsequently annealing. The length of the nanotubes decreases with increasing anodization temperature from about approximately 15 μm at 40 °C to approximately 4.5 μm at 60 °C. High resolution transmission electron microscope images and selected area electron diffraction pattern confirm the polycrystalline anatase specimen consisting of many nanocrystals with a random orientation.

1. Introduction

In 2001, Gong et al. [1] pioneered the synthesis of the first generation TiO_2 nanotube arrays of up to 500 nm length by electrochemical of titanium in a HF aqueous electrolyte. And then Cai et al. [2] adjusted the pH of the electrolytes to increase the nanotube length to over 6 μm. Hereafter, various organic electrolytes, such as formamide, ethylene glycol, and dimethyl sulfoxide [3–5] containing fluoride ions, have been utilized to fabricate nanotube arrays of greatly extended length. Even in 2007, Paulose et al. [6] succeeded in fabricating 1000 μm thick TiO_2 nanotube arrays used ethylene glycol as electrolyte.

TiO_2 nanotube arrays have found potential applications in semiconductor devices [7], photovoltaic cells [8,9], and carrier of catalysts [10,11] due to its novel microstructure and high specific surface areas. Titania minerals are found in three different crystallographic structures: anatase, rutile and brookite. Although some applications such as normal solution filtering do not require crystalline membranes, crystallinity is essential when biocompatible, photocatalytic, or semiconducting properties are desired [6]. For example, anatase phase titania is preferred in dye sensitized solar cells and catalysis, whereas rutile is mostly used in the area of dielectrics and high temperature oxygen gas sensors [12]. As far as we know, the as-fabricated titania nanotube arrays are amorphous [13]. To convert the amorphous tubes into crystalline anatase or rutile phase, usually annealing is necessary [14,15]. Because annealing operations at several hundred degrees Celsius are necessary for this anodization process, a large amount of energy is consumed in the formation of the crystalline titania nanotubes and it is impossible to form the anatase nanotube arrays on lower thermostability material substrates. In this study, the apparent polycrystalline anatase nanotube arrays are fabricated in dimethyl sulfoxide electrolyte containing HF aqueous solution at 50–60 °C, which is interesting and promising.

2. Experimental

Prior to anodization, titanium sheets (99.5% pure) were ultrasonically cleaned, respectively, in acetone and distilled water, and then eroded in 4 wt%HF + 5 mol/L HNO_3 for 30 s. Titania nanotube arrays were prepared by anodization of the Ti foils in 50 mL dimethyl sulfoxide (DMSO) + 1 wt% hydrofluoric acid mixed electrolytic solution. A two electrode configuration was used for anodization. A flag shaped platinum electrode serves as cathode. The whole course of anodization was conducted at 40 V with a

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DH1719A-4 power supply for 24 h. The temperature of the solution was kept at 40–60 °C.

Philips XL30 environmental scanning electron microscope (ESEM) was employed for the structural and morphological characterization of the sample. X-ray diffraction (XRD) measurements were performed on Philips X'Pert MPD diffractometer with Cu Kα radiation. The high resolution transmission electron microscope images (HRTEM) and selected area electron diffraction (SAED) of individual nanotube were performed by using a FEI Tecnai G2 F20 S-TWIN microscope at an acceleration voltage of 200 kV.

3. Results and discussion

3.1. Morphology of nanotube arrays

Fig. 1(a)–(c) shows the ESEM images of the morphology of titania nanotube arrays fabricated at 40 V at different temperature.

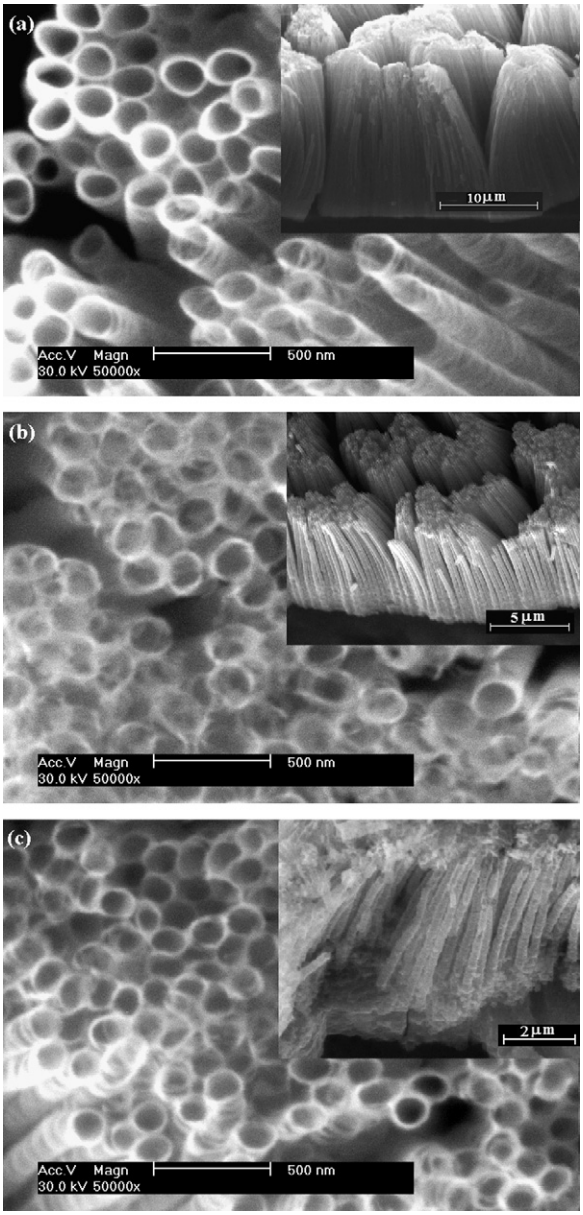

Fig. 1. ESEM images of titania nanotube arrays anodized at different temperature: (a) 40 °C; (b) 50 °C; (c) 60 °C. The insets show the cross-sectional views.

The corrugated structure of nanotube walls can be seen in Fig. 1, this should be addressed to the presence of water in HF aqueous, resulting in the concentration fluctuations and pH bursts during anodization [16]. The vertical alignment of the nanotubes and general morphology are independent of the temperature used. The pore diameter are nearly the same for the 40 V anodized titania nanotube arrays fabricated at different temperatures, whereas the tube length has changed. The length of the nanotubes decreases with increasing anodization temperature from about approx. 15 μm at 40 °C to 6.5 μm at 50 °C and approx. 4.5 μm at 60 °C (as shown in the inset of Fig. 1(a)–(c)). The changes can be explained through the formation mechanism of titania nanotubes. The fundamental formation of nanotube arrays in fluoride containing electrolytes is the result of three simultaneously occurring processes: the field assisted oxidation of Ti metal to form titanium dioxide, the field assisted dissolution of Ti metal ions in the electrolyte, and the chemical dissolution of TiO_2 due to etching by fluoride ions [17,18]. The formation of nanotubes in an aqueous HF containing electrolyte is described by a localized dissolution model [4,17,18] via the following reactions:

$$Ti + 4H_2O \rightarrow TiO_2 + 4H^+ + 4e \quad (1)$$

$$TiO_2 + 6F^- + 4H^+ \rightarrow [TiF_6]^{2-} + 2H_2O \quad (2)$$

For organic electrolytes, the fundamental growth mechanism is generally the same, but the donation of oxygen is more difficult in comparison to water and results in a reduced tendency to form oxide. The nanotube length depends on the competition between the chemical dissolution rate of the oxide at the pore mouth and the growth rate of oxide at the bottom of the pore. Wet chemical etching is a temperature dependent process, with etch rates typically being exponential functions of the temperature. The solubility product of ions in any given electrolyte is also a strong function of temperature [19]. It is therefore reasonable to assume that the chemical dissolution rate of the oxide will be faster at higher temperatures, thus accounting for the shorter tube length. Fig. 2 shows the time dependent anodization current density at different temperature. During the process of anodization, with the increase of the temperature, the conductivity and ions movement velocity of the electrolyte will increase, resulting in higher current density. The steeper slope at higher temperature seen in Fig. 2(c) is attributed to the faster rate of chemical dissolution which make the length of the titania nanotube arrays much shorter.

Ge Ruixia et al. have studied the influence of temperature on the size of titania nanotube arrays in 0.5% HF + acetic acid mixed in a

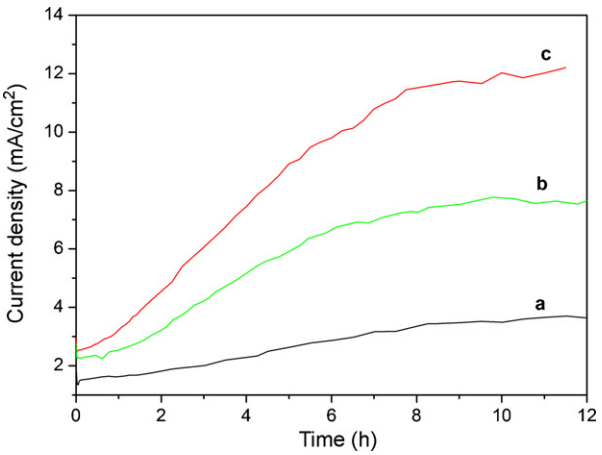

Fig. 2. Current density versus time behavior during anodization of Ti at different temperature: (a) 40 °C; (b) 50 °C; (c) 60 °C.