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Controlling anodization time to monitor film thickness, phase composition and crystal orientation during anodic growth of TiO₂ nanotubes

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ARTICLE INFO	A B S T R A C T
Keywords: TiO ₂ nanotube arrays Anodic oxidation Phase transition and composition Growth curve Sigmoidal growth model	Anodic TiO ₂ nanotube (TNT) films show promises for photon-driven catalytic, electricity storage and chemical processes. The film thickness of anodic TNT is known to affect its performance in optical and electronic applications. Also, factors affecting the morphology and dimensions of anodic TNT films are rather well-known. However, the knowledge on phase transition and composition in the growth of anodic TiO ₂ from the titanium metal is very limited. In this work, the anodization time is controlled in intervals of 10, 60, 300, 1000, 2000 and 5000 s to investigate its effect on phase composition and transition, and the morphology of the anodic TNT during the growth process. Even though the mechanism of anodic TNT formation is still under debate, the scanning electron microscope results support bottom-up tube growth with evidence of a compact layer. It was also found that the Richards growth model is applicable to correlate growth time and film thickness. Finally, the

1. Introduction

Anodic TiO₂ nanotube (TNT) material finds applications in many energy processes including water (H₂O) splitting into hydrogen and oxygen [1], carbon dioxide reduction [2] and nitrogen reduction reactions [3–5]; and in energy storage and transformation devices e.g., dye sensitized solar cells [6], ion batteries [7], supercapacitors [8] and fuel cells [9].

The electric and optical behavior of anodic TNT strongly depends on its morphology, phase composition and crystal facet arrangement [1]. The thickness, as an important parameter of morphology, affects its performance. Many studies have reported on controlling the anodic TNT dimensions, e.g., the tube length, inner diameter and wall thickness [10–15]. The effects of preparation factors, such as titanium (Ti) foil size [1], H₂O concentration [10], the source and concentration of fluoride ion (F) [10], the pH of the electrolyte [16], the applied voltage or current [17], and the nature of solvent, e.g., ethylene glycol (EG) [15], dimethyl sulfoxide [13], and glycerol [11], the reaction temperature and time [16], etc. on the tube morphology [16] have been examined. Anatase or rutile, the two main crystal polymorphs of TiO₂, are often formed during the annealing process [18]. Each polymorph exhibits its own electric and optical properties, resulting in different applications. Rutile is the most thermodynamically stable phase under ambient conditions while anatase is metastable at all temperatures. Moreover, welldefined TiO_2 facets have been achieved in anatase crystallites. For example, the high reactive (001) facet of anatase TiO_2 in solar-to-fuel devices has been intensively investigated [19].

phase transition, crystal orientation and pore formation during the anodic process are further discussed.

The growth rate of the anodic TNT film thickness or the tube length is a highly relevant research topic [20–22]. Zhang *et al.* [20] correlated the growth rate of anodic TNT as a function of applied voltage and the reaction temperature. Zhao *et al.* [23] derived a mathematical model of voltage–time transient curves based on the oxygen bubble mould effect model to calculate the anodic TNT growth rate under constant current conditions.

In this work, the effects of anodization time on the phase composition and transition and the morphology, i.e. film thickness and the top view of the surface, of the anodic TiO_2 films are investigated. Moreover, a growth model is proposed to describe the relationship of anodization time and film thickness.

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2. Experimental

2.1. Fabrication of anodic TiO₂ nanotubes

The samples were fabricated with the anodic oxidation method in a two-electrode setup with a Ti foil (purity = 99.5%, thickness: 0.02 cm, Beijing Zhongnuo Advanced Material Technology Co., Ltd.) as the working electrode, and Pt foil (purity > 99.99%, Tianjin Aida Hengsheng Technology Development Co., Ltd.) as the counter electrode in an electrolyte of a mixture of 0.3 wt% ammonium fluoride (NH₄F, ACS reagent, \geq 98.0%, Sigma-Aldrich) and 6 vol% deionized H₂O in EG (HOCH₂CH₂OH, anhydrous 99.8%, Sigma Aldrich and Merck). The setup was powered by a DC supply of 60 V at ambient condition. The anodization time for the growth of anodic TNT film was set for 10, 60, 300, 1000, 2000 and 5000 s, followed with a post annealing treatment at 450 °C for 30 min with a heating rate of 3 °C/min in a muffle oven (Nabertherm, Germany) in air. The six samples were noted as 10s, 60s, 300s, 1000s, 2000s and 5000s.

2.2. Characterization

The morphology was observed with a DualBeam focused ion beamscanning electron microscope (FIB-SEM, Jeol 4700F). Prior to FIB, a carbon layer was pre-deposited on the top of the sample for protection against beam damage. The structure was characterized with X-ray diffraction (XRD) (PANalytical X'PertPro) using Cu-K α ($\lambda = 1.540598$ Å) radiation under 40 kV, 40 mA.

3. Results

3.1. Anodization time control

Fig. 1(a) shows the transient *i*-log(*t*) curve recorded during anodization process under a constant voltage of 60 V [1]. The curve has 5 parts reflecting the transition between the different growth kinetics, two zero-order reaction cycles (II and IV) and three first-order reaction intervals (I, III and V). This current curve can be well explained with the electronic current and oxygen bubble model [24,25]. The 6 samples were taken after TiO₂ film growth falling in the different time intervals as marked in Fig. 1(a). The photos of the 6 samples after post annealing are presented in Fig. 1(b), and the physical appearance of the samples are obviously different from each other.

3.2. Effect of anodization time

3.2.1. Effect on phase composition and crystal orientation

The XRD patterns of the samples are presented in Fig. 2, which show clearly the phase transition from Ti metal to TiO₂ anatase phase along with the anodization time. In the samples of 10s and 60s, the XRD patterns only exhibit the peaks of hexagonal closely packed Ti metal α -phase (JCPDS no. 44–1294). The 300s sample firstly exhibits the characteristic peak A (101) of anatase phase (JCPDS no. 21–1272). For sample 1000s, the A (004), A (200), and A (105) peaks of anatase phase appear. When the time was increased to 2000 s, the A (103), A (211), A (204), A (116) and A (215) peaks are monitored with the XRD technique. Further increase the anodization time, the number of peaks of anatase does not change. The relative intensities of both T (002) at 38.42° and T (103) at 70.66° are enhanced and show a monotonic increasing with the increase of the anodization time. The peak intensity of T (200) of the Ti foil used in this work, see Fig. S1, is lower than that in the XRD patterns for Ti (JCPDS, 44–1294) and the value does not



Fig. 2. The XRD patterns of the samples: 10s, 60s, 300s, 1000s, 2000s and 5000s. A: anatase TiO_2 and T: Ti metal



Fig. 1. The anodic growth i-log(t) curve at 60 V [1], and photos of the six samples.

change much along with the increase of the anodization time. For the anatase phase, with the increase of the anodization time from 300 to 5000 s, the relative intensities of the A (101), A (200), and A (105) peaks increase. However, the other anatase peaks do not show enhancement along with the increase of the anodization time. Moreover, among the three peaks, the relative intensity increase has an order A (101) > A (200) > A (105).

3.2.2. Effect on the film thickness

Fig. 3 gives the FIB-SEM images of the 6 samples to show the film thickness. Increase of the anodization time leads to an increase of the film thickness. The 0s, 60s, 300s, 1000s, 2000s and 5000s samples have thicknesses of 0.072, 0.090, 0.480, 1.75, 5.51, and 9.75 μ m, respectively.

From the growth curve in Fig. 4, we are informed that during 1000–3000 s the film growth rate of is the fastest. The growth rate is slow in both the 0–60 s and 3500–5000 s time intervals. The curve has a sigmoidal shape. Therefore, the SRichards2 growth model was used to fit the experimental data and find a high fidelity to the experimental curve in Fig. 4, *viz*, $R^2 = 0.999$ (R^2 , goodness of fit). Based on the growth model, a mathematical model was derived to describe the growth tendency of the film thickness affected by the anodization time, i.e. equation (1)

$$y = a^{*} \left(1 + (d-1)^{*} exp(-k^{*}(x-xc))^{\frac{1}{1-d}} \right); \quad x = 0 - 5000s$$
⁽¹⁾

in which $a = 9.92 \pm 0.16$, $xc = 1.60 \times 10^3 \pm 98.1$, $d = 1.19 \pm 0.22$, $k = 1.19 \times 10^{-3} \pm 1.86 \times 10^{-4}$.

The Richard growth model here does not correlate with a mechanism. However, it is useful to predict the anodic TNT film thickness, which is an important factor in many applications such as dye solar cells, perovskite solar cells, and the photoelectrochemical water splitting cells.

3.2.3. Effect on the top surface morphology

The zoom-in SEM top view of the 6 samples is shown in Fig. 5. At 10 s, nanoparticles are observed on the top surface, which are likely formed due to the dissolution. The sample shows a blue color appearance in Fig. 1(b). In the sample taken at 60 s, countable pores marked with yellow circles, appear as illustrated in Fig. 5(b). In the 300s sample, more pores are visible and are widened. In the three samples taken during 1000–5000 s, the pores become uniformly distributed on the



Fig. 4. The correlation of film thickness and anodization time with a Richards growth model (dotted line).

surface.

The details of the top surface are observed with the SEM. The micrographs are given in Fig. 6. The 10s sample exhibits, Fig. 6(a), as a compact film with dots/particles on the surfaces. In Fig. 6(b), the SEM of the 60s sample gives smaller size particles and the pores become visible, which is in agreement with the observation in Fig. 5(b). Pores in Fig. 6 (c), for the sample taken at 300 s, have different sizes. Spherical particles, with diameters in a range of $70 \sim 315$ nm, are observed. For the sample taken at 1000 s, a dense layer, ca. 100 nm, without pores is observed on the top of the tubular film. For the two samples obtained at 2000s and 5000s, Fig. 6(e) and (f), the dense layer is no longer existing. However, the tubes show a two-layer structure of the nanotubes with the top layer different from the main body tube film layer, demonstrating that the growth of the nanotubes takes place in a bottom-up way due to the oxide flow around the oxygen bubble mold [26]. The top layer seems formed due to the etching of the dense layer shown in Fig. 6(d).



Fig. 3. The FIB-SEM micrographs of the cross-sectional view of the samples: (a)10s, (b) 60s, (c) 300s, (d)1000s, (e) 2000s and (f) 5000s.



Fig. 5. Top view of the six samples from the Zoom-in of Fig. 3.



Fig. 6. The SEM micrographs of the top view of the samples: (a)10s, (b) 60s, (c) 300s, (d)1000s, (e) 2000s and (f) 5000s.

4. Discussion

4.1. Phase transition and crystal orientation

The XRD results in Fig. 2 show that the peaks of the anatase TiO_2 phase appear in groups and with a sequence of group 1, A (101); group 2, A (004), A (200) and A (105); and group 3, A (103), A (211), A (204), A (116) and A (215), which indicates the preferential growth of the anatase phase. The XRD patterns of the Ti-metal phase exhibit distortion along the T (002) and T (103) directions showing a remarkable enhancement of the comparative intensities of the two peaks with the increase of the anodization time. Besides, it has been reported that the post-annealing temperature affects the phase composition and transition of anodic TNT, viz, amorphous, anatase and rutile phases [27]. Without post-annealing treatment, anodic TNT will not show interesting electronic and optical properties for applications.

The facet preferential directional growth of a phase is attributed to the optimization of the surface energy during the process. Thermodynamically stable (101) facet of anatase dominates the crystal growth, which has been already noticed in literature [19]. In this work, the (101) facet forms first and the relative intensity of A (101) peak increases with the increase of the anodization time. However, the facet preferential direction of Ti metal phase has been ignored. The T (200) peak in the pattern of the Ti foil and those of all the six samples are much lower than that in the JCPDS card, which is attributed to the effect of the native self-formed TiO₂ oxidation layer on its surface [28]. Besides, (200) may be the most active facet to form the surface passivation layer of Ti metal. During the initial 10 s, before the formation of detectable anatase phase, the relative intensity of both T (002) and T (103) are already enhanced and further strengthened in the following period under the strong electrical field, 60 V.

4.2. Pore formation

The XRD results in this work do not support the formation of TiO_2 dense layer during the initial 10 to 60 s, even though the FIB-SEM observed the film thickness in the range of 70 to 90 nm. As shown in Fig. 5(a) and Fig. 6(a), the SEM of the 10s sample has a textured surface, indicating the dissolution process of the top-surface during the initial 10 s. Next, following with the observation of very few countable pores on

Fig. 5(b) and Fig. 6(b), meaning the porous formation was started before the anodization time of 60 s. When anodization time increases to 300 s, the pores on the top surface take a certain percentage. As shown in Fig. 7, the cavities dig with the diameter in the range of 70–320 nm and the same to the leaving nanoparticle sizes on the surface. Based on the observations in Fig. 5 and Fig. 6, the phenomena in Fig. 7 is a result of ions etching and dicing. When the anodization time interval is 1000–5000 s, the tube inner and outer walls and the tube length are observed. Interestingly, Zhou *et al.* [24] were against the F⁻ ions field assisted dissolution mechanism, as they observed nanotube formation in EG electrolyte while only dense TiO₂ film forms without tube in the ethanol electrolyte, even though the anodizing current–time curves obtained in ethanol electrolyte are similar to those obtained in EG. The formation of the pores may therefore need further investigations.

5. Conclusions

In summary, six anodic TiO₂ samples were prepared by controlling the anodization time with time intervals of 10, 60, 300, 1000, 2000 and 5000 s, which were showing different physical appearance after annealing process. The anodization time had an effect on the crystallinity and phase composition and film thickness of anodic TNT. The phase information was checked by XRD, which revealed that the sequence of the appearance of the anatase peaks and an order of the increase of the relative intensity of the anatase peaks. Further, the distortion of Ti metal phase during the growth of anodic TiO₂ form Ti metal was also monitored with controlling the anodization time. The effect of anodization time on the film thicknesses was measured by FIB-SEM, which was well fitted with a SRichard2 model ($R^2 = 0.999$). Top surface changes/development with increasing anodization time were also observed by SEM, from the surface textures to the formation of pores/tubes, next to the uniform tube surface with co-existence of navies, further to the uniform tubes. The phase transition and orientation during the growth of anodic TNT and the pore formation were further discussed.

CRediT authorship contribution statement

Xuelan Hou: Methodology, Investigation, Visualization, Writing – original draft. Peter D. Lund: Writing – review & editing, Supervision. Yongdan Li: Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial



interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.elecom.2021.107168.

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Fig. 7. The SEM top view of the sample 300s.

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