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Formation Mechanism of Lotus-root-shaped Nanostructure during Two-step Anodization

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ABSTRACT

Anodic TiO_2 nanotubes (ATNTs) have been widely investigated due to their interesting formation mechanism. The general accepted mechanism is the field-assisted dissolution theory. Here, two-step anodization processes under different voltages and various lotus-root-shaped nanostructures have been studied in detail. When the applied voltage of second anodization is the same as that of first anodization, lotus-root-shaped nanostructure is found for the first time. These lotus-root-shaped nanostructures of ATNTs can not be elucidated by the field-assisted dissolution. Based on the oxygen bubble mould and the oxide flow model, new explanation for the lotus-root-shaped nanostructure is presented. The anion contaminated layer (ACL) formed around the residual concaves plays critical roles in the formation of lotus-root-shaped nanostructure. When the hexagonal stripes and the mesh-like coverage of anion contaminated layer covered on the nanotubes disappear, the lotus-root-shaped nanostructures will vanish away.

1. Introduction

Anodic TiO_2 nanotubes (ATNTs) have been widely investigated due to their various applications [1–4] and interesting formation mechanism [5–8]. The fabrication and formation mechanism of ATNTs have received considerable attention in recent years [5–11]. The general accepted mechanism is a field-assisted dissolution ($TiO_2 + 6F^- + 4H^+ \rightarrow [TiF_6]^{2-} + 2H_2O$) process for the pore formation in anodic titania films [6,7,10,11]. However, Chang and Hu et al. [8,9] reported that nanotubes or nanoporous oxide were fabricated by anodization of Ti and its alloy in $AgNO_3$ and HNO_3 solutions without fluoride. ATNTs have also been achieved in H_2SO_4 solution as well as other fluoride free solutions [10]. These facts put the field-assisted dissolution or the fluoride effect ($[TiF_6]^{2-}$) into question [8–10]. As Hebert et al. [12] indicated that the relationship between structural features and processing parameters was not yet well explained. No matter for porous anodic alumina or anodic titania films, they proposed that pore initiation maybe result from the morphological instability and the nonlinearity of ionic conduction [12,13]. More recently, they suggested that pores are created by a flow instability caused by spatially nonuniform near-surface compressive stress [14]. In fact, despite the intensive investigation and much deeper interpretation on the formation of ATNTs, there are still some problems remained to be solved [10,11,14]. In a two-step anodization process for titanium, the patterned Ti substrate left by the first anodization fails to guide pore growth in the second anodization [10]. Some special nanostructures with lotus-root-shaped obtained in porous anodic titania and alumina films provide evidence for the conclusion above [15–17]. Besides, the exact origin for the gap formation between nanotubes still requires further investigation [10,11]. In order to fully understand the formation mechanism and control the morphology of ATNTs, it is of great importance to overcome the above problems [10,13,14].

Based on the 'plastic flow' model [12–14,18,19] and the avalanche breakdown theory [20–23], the 'oxygen bubble mould' [24–26] and the electronic current model [22,24,27] were proposed to explain the relationship between nanotube morphology and current density-time curve. These models were improved by their subsequent work [28–30]. The nanotube embryos which result from the oxide flow around the oxygen bubble remained within the film [29]. The oxygen bubble is the precondition of the oxide flow from the pore base to the pore wall [29,30]. These viewpoints have received a lot of attention and citation [31–39]. The viewpoints help to explain many problems, for example, the formation mechanism of the gaps and ribs around the nanotubes was elucidated by the oxygen bubble mould rather than by the field-assisted dissolution [30].

It is well known that the lotus-root-shaped nanostructure in porous anodic titania and alumina is formed in two-step anodizing process of Ti and Al [15–17]. However, to the best of our knowledge,

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there are very few papers concerning the formation mechanisms of lotus-root-shaped nanostructure. In this paper, we focus on the forming process of ATNTs with lotus-root-shaped nanostructure. In different two-step anodizations, diverse morphologies of ATNTs formed under different anodizing voltages were investigated in detail by the field-emission scanning electron microscope (FESEM). Lotus-root-shaped nanostructures with several small holes contained in each concave were obtained under different conditions. The evolution and disappearance of lotus-root-shaped nanostructure were discussed. And a new mechanism for the growth of the nanotubes with lotus-root-shaped nanostructure is proposed on the basis of the previous literature.

2. Experimental details

The commercial titanium foil (100 μm thick, purity 99.5%, Shanghai Shuangmu Technology Co. Ltd.) was used as a working electrode and platinum mesh served as a counter electrode. The titanium foils were polished using a mixture solution of HF (≥40%, Shantou West Long Chemical Factory Limited), HNO_3 (65-68%, Shantou West Long Chemical Factory Limited) and deionized water (1:1:2 in volume) for 8–10 s. Subsequently, the samples were rinsed thoroughly by deionized water and dried in the air before being anodized. The pretreated samples were all anodized in ethylene glycol solutions containing 0.5 wt% NH_4F (no extra water was added) at 20 °C. The current density-time curves during anodizing were recorded automatically by a computer measurement system. In the first step, the polished Ti foils were anodized under 40 V for 30 min. Then the as-anodized Ti foil was ultrasonically rinsed in deionized water for 10 min to remove the formed TiO_2 nanotubes to obtain the patterned Ti substrate. After being washed and dried in the air, the as-prepared Ti substrates were anodized for the second time in the aged electrolyte; the temperature and electrolyte were the same as those of the first step. However, the second anodization was carried out under different voltages and durations. The surface morphology of the nanotube arrays obtained from the second anodization was investigated. All samples were examined by FESEM (Zeiss Supra 55 and Hitachi S-4800). Nanotube diameter was measured directly on the FESEM.

3. Results and discussion

3.1. Morphologies of nanotubes obtained in one-step anodization

Fig. 1 shows the FESEM images of the ATNTs obtained by one-step anodization in ethylene glycol solution containing 0.5 wt% NH_4F. The anodization was performed under constant voltage (40 V) for 30 min. Fig. 1a and 1b show the porous surface morphology and the cross-section morphology of ATNTs. The lotus-root-shaped nanostructures can not be found on the surface of the sample after the first anodization.

The sample with ATNTs was ultrasonically rinsed in deionized water for 10 min to peel off the formed nanotubes. The inset of Fig. 1c shows the formed nanotubes in the first anodization. After being peeled off the formed nanotubes, the Ti substrate with ordered concaves is shown in Fig. 1c. The diameter of residual concave is about ~103.8 nm. The approximate diameter of nanotube is ~90.4 nm as shown in Fig. 1b. It means that there is a one-to-one correspondence between residual concaves and nanotubes obtained in the first anodization. The patterned Ti substrate shown in Fig. 1c is ready for the second anodization.

3.2. Lotus-root-shaped nanostructure obtained in two-step anodization

Fig. 2 shows the surface morphology and cross-section morphology of nanotubes after the second anodization, in which

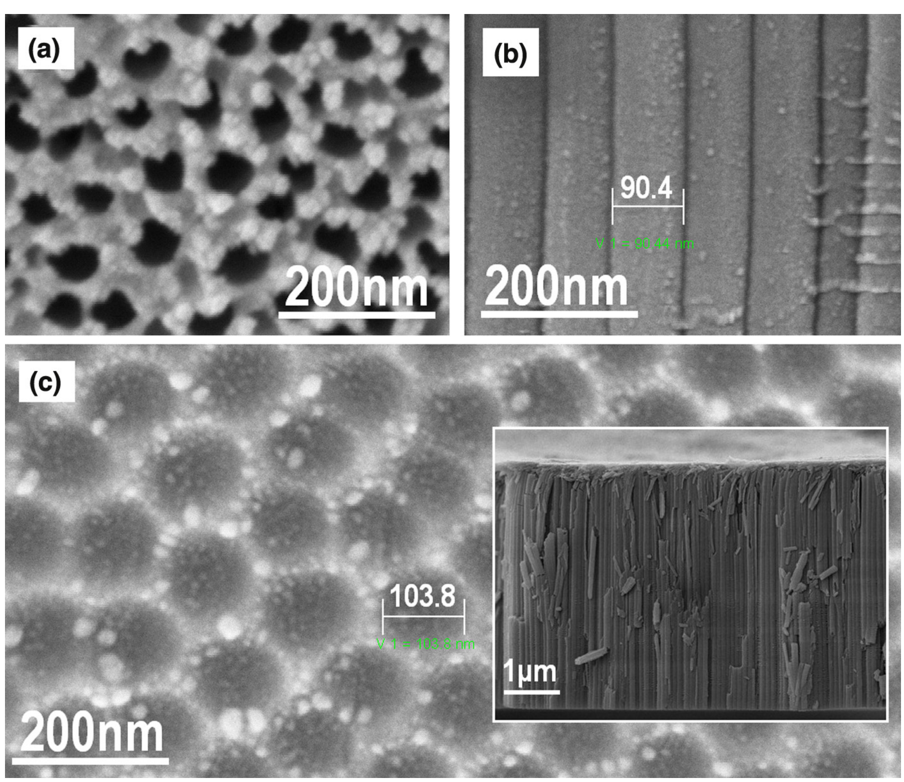

Fig. 1. FESEM images of the ATNTs anodized at 40 V for 30 min, (a) the surface morphology, (b) the cross-section morphology, (c) the residual concaves on the Ti substrate after the removal of nanotubes formed in the first anodization, the inset showing the whole cross-section morphology of nanotubes formed in the first anodization.