

RAPID COMMUNICATIONS

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Titanium oxide nanotube arrays prepared by anodic oxidation

Dawei Gong, Craig A. Grimes,^{a)} and Oomman K. Varghese

Department of Electrical Engineering and Materials Research Institute, 208 Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802

Wenchong Hu, R.S. Singh, and Zhi Chen

Departments of Material Science and Engineering, and Electrical Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802

Elizabeth C. Dickey

Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802

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Titanium oxide nanotubes were fabricated by anodic oxidation of a pure titanium sheet in an aqueous solution containing 0.5 to 3.5 wt% hydrofluoric acid. These tubes are well aligned and organized into high-density uniform arrays. While the tops of the tubes are open, the bottoms of the tubes are closed, forming a barrier layer structure similar to that of porous alumina. The average tube diameter, ranging in size from 25 to 65 nm, was found to increase with increasing anodizing voltage, while the length of the tube was found independent of anodization time. A possible growth mechanism is presented.

Titanium oxide is a useful catalytic¹ and gas-sensing² material. Titanium oxide thin films with nanoporous structures are desirable for these applications due to their large surface areas and high reactivities. Nanoporous titanium oxide films have been fabricated by anodizing titanium sheets in hydrofluoric acid containing solutions.^{3,4} The anodizing approach is able to build a porous titanium oxide film of controllable pore size, good uniformity, and conformability over large areas at low cost.⁵ Moreover, as dependent upon the titanium alloy used, metal impurities can be readily introduced. Despite these advantages, there is a dearth of literature on anodization of titanium and titanium-based alloys. Our work is aimed toward better understanding of the anodizing mechanism, as well as the fabrication of new nanodimensional structures for possible application in catalytic, biotemplating,^{6,7} gas-sensing⁸ and electronic applications.

In this work, we examine the morphology of porous titanium oxide thin films fabricated by anodizing pure titanium sheets under variable conditions. It has been found that the anodized titanium films have more complicated morphologies than anodized aluminum.⁹ In

addition to porous films, such as those reported earlier,³ well-aligned nanotubelike structures composed of titanium oxide were obtained. In contrast to the continuous pore structures achieved with aluminum anodization, discrete titanium oxide nanotubes are found to grow from the discontinuous nanoporous titanium oxide film.

The high-purity (99.99%) titanium foils used in this work were obtained from Alfa Aesar (Ward Hill, MA).¹⁰ All anodization experiments were conducted at room temperature (18 °C) with magnetic agitation. The anodizing voltages were kept constant during the entire process. In the first 5–10 s of the anodization the currents were observed to decrease drastically and then afterwards remained stable. During anodization the color of the titanium oxide layer normally changed from purple to blue, light green, and then finally light red. The morphologies of the titanium oxide films were characterized with a Hitachi S-900 (Tokyo, Japan) field emission scanning electron microscope (FE-SEM).

Figures 1(a)–(d) show, respectively, FE-SEM images of the porous structures obtained with different anodizing voltages, 3, 5, 10, and 20 V, in 0.5 wt% HF aqueous solution. At low anodizing voltage [see Fig. 1(a)] the morphology of the porous film is similar to that of porous (spongelike) alumina,⁹ with a typical pore size of 15 to

^{a)}e-mail: cgrimes@enr.psu.edu

30 nm. As the voltage is first increased, the surface becomes particulate, or nodular, in nature, as shown in Fig. 1(b). As the voltage is further increased, the particulate appearance is lost, with discrete, hollow, cylindrical, tube-like features appearing [see Figs. 1(c) and 1(d)]. The nanotube structure is lost at anodizing voltages greater than 40 V, and a spongelike randomly porous structure is formed. A

similar evolution of topological features was also observed in a 1.5 wt% HF solution at lower voltages; the reduced voltages did not scale linearly with solution concentration.

To our knowledge the tubelike structures of anodized titanium observed in Figs. 1(c) and 1(d) have not previously been reported. Cross-sectional FE-SEM images of a titanium oxide nanotube array are shown in Figs. 2(a)

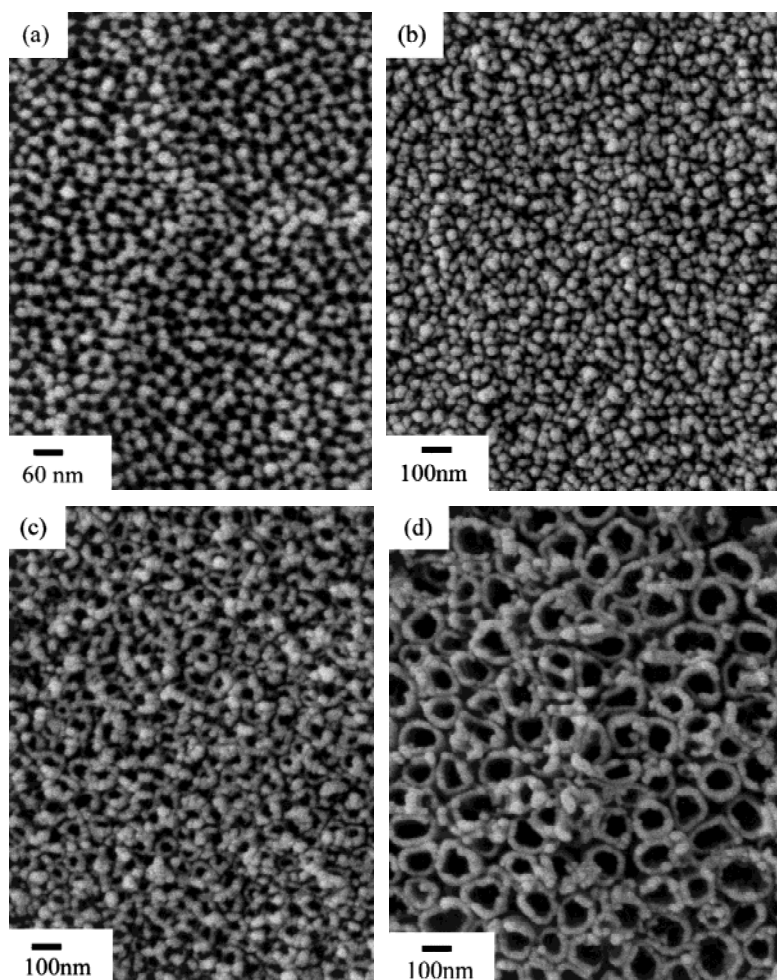


FIG. 1. FE-SEM top-view images of porous titanium oxide films anodized in 0.5 wt% HF solution for 20 min under different voltages: (a) 3 V, (b) 5 V, (c) 10 V, and (d) 20 V.

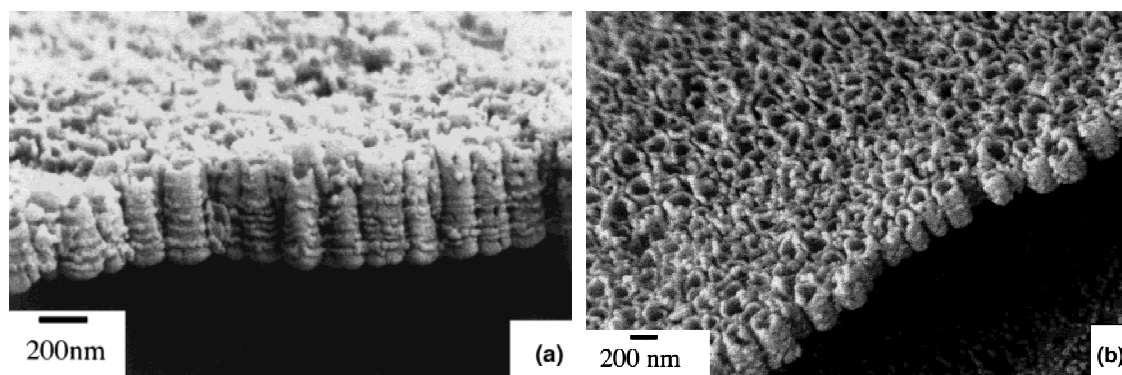


FIG. 2. FE-SEM cross-sectional images of titanium oxide nanotubes. The sample was anodized in 0.5 wt% HF solution at 20 V for 20 min.

and 2(b). This sample was anodized at 20 V in 0.5 wt% HF solution for 20 min, resulting in a well-aligned titanium oxide nanotube array with an approximately average tube diameter of 60 nm and tube length of 250 nm. It is interesting to note that the tube exteriors show periodic ring structures, the origin of which we are uncertain. Glancing-angle XRD showed the resulting titanium oxide structures to be amorphous. The underside of the nanotube-array films (see Fig. 3) were imaged by first fracturing the sample and then peeling the films from the substrate. The domelike nature of the underside is identical to the so-called barrier layer, a thin oxidized layer separating the porous layer from the metal substrate, commonly seen with porous alumina.⁹

In our experiments, the titanium oxide nanotube arrays were regularly obtained under anodizing voltages ranging from 10 to 40 V, as dependent on the HF concentration, with relatively higher voltages needed to achieve the tubelike structures in more dilute HF solutions. In all cases, the final length of the nanotubes was found to be independent of the anodizing time.

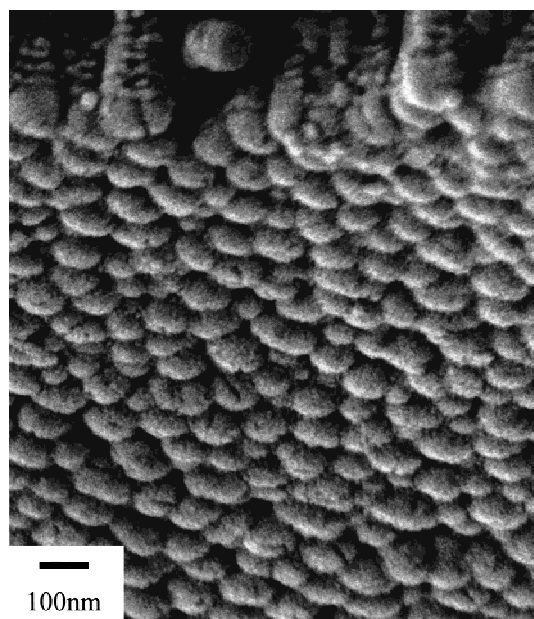


FIG. 3. Fe-SEM image of the bottom of the nanotube array. The sample was anodized in 0.5 wt% HF solution at 20 V for 20 min.

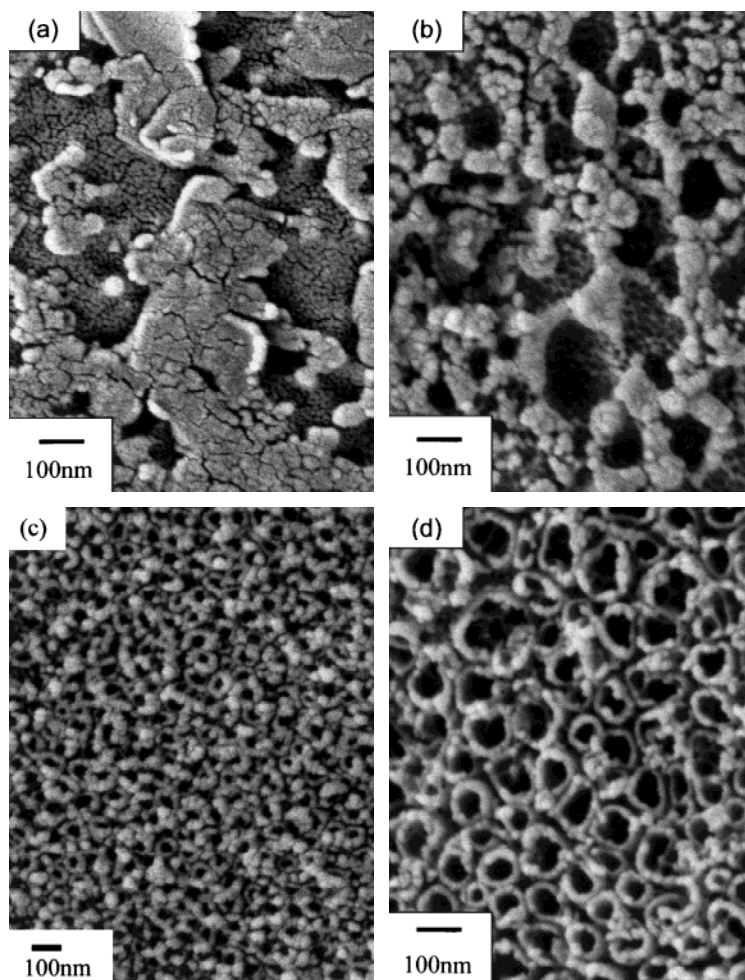


FIG. 4. FE-SEM top-view images of porous titanium oxide films anodized in 1.5 wt% HF solution at 20 V for different times: (a) 10 s, (b) 30 s, (c) 120 s, and (d) 8 min.

It is well known that during the anodization of aluminum, porous structures are formed through two processes: field-enhanced oxidation of aluminum and field-enhanced oxide dissolution.¹⁰ Inside the pore channel there are two interfaces: solution/oxide and oxide/metal. Field-enhanced oxidation occurs at the metal/oxide interface near the pore bottom when the oxygen containing ions (O^{2-}/OH^-) transport from solution to the oxide layer, along the direction of the pore growth. At the same time, metal ions (Al^{3+}) migrate from metal to the solution/oxide interface and dissolve into the solution. Since the electric field can enhance the migration of the metal ion, the later process is called field-enhanced dissolution. As the electrical field intensity at the pore bottom is much higher than that at the wall, aluminum will be consumed at a high rate near the bottom of the pore, allowing continuous growth of the pore depth. In contrast, for anodized titanium the final thickness of porous oxide film does not increase with the anodizing time. For example, we find that a sample anodized in 0.5% HF solution under 20 V for 6 h has the same thickness as a sample anodized for only 20 min under otherwise identical conditions, a result consistent with earlier work.³ The origin of this behavior may lie in the fact that titanium oxide can be etched at a high rate in HF solution even in the absence of an anodizing voltage. If the etching rate of the oxide in solution is comparable with that of the field-enhanced dissolution, the titanium oxide either in the wall or at the pore bottom will dissolve at a balanced rate resulting in a constant pore depth.

To further understand the formation of the nanotube-like structures during anodization of titanium, FE-SEM images were taken from a series of samples fabricated using 20 V in 1.5% HF solution with different anodizing times. The evolution of the film morphology is shown in Fig. 4. It is found that at the initial stage, within 10 s, the surface was covered with a compact oxide film, of uneven height, as shown in Fig. 4(a). After 30 s [see Fig. 4(b)], the original oxide film is clearly dissolving with a continuous nanoporous layer emerging from underneath without any indication of tubelike features. With further anodization [see Fig. 4(c)], most of the original oxide film layer is removed, replaced by a film comprised of emerging discrete tubelike structures. After an elapsed anodization period of 8 min, all vestiges of the original oxide film were completely removed and a continuous film of discrete nanotubes fully developed on the surface. The time-dependent transitions were confirmed by cross-sectional FE-SEM images taken from the corresponding samples. In all cases, the nanotubelike structures were seen to develop from the porous structure formed during removal of the initial surface oxide layer.

One possible process contributing to the formation of the nanotube structures during anodization is the migration of titanium ions from the interpore areas to the oxide/solution interface. At high anodizing voltages, the electric field will be strong enough to mobilize these ions and their migration leaves voids in the interpore areas, eventually separating the pores from one another, forming discrete tubelike structures. Such a field-enhanced void structure was previously observed under the barrier layer of an anodized aluminum oxide film upon a silicon substrate.^{11,12}

To help examine the influence of solution composition on the titanium oxide nanostructures, 1 g chromium trioxide was added to 100 ml 0.5 wt% HF solution. The results show the nanotube arrays formed under 20 and 40 V in this mixed electrolyte have the same diameters as those anodized in pure 0.5 wt% HF solution under 10 and 20 V, respectively. Certainly solution composition has a significant affect on process variables; further research is needed to find the optimum anodizing conditions to achieve optimal arrays of titanium oxide nanotubes.

In conclusion, well-aligned titanium oxide nanotube-like arrays have been obtained through titanium anodization in HF solution. The resulting nanotubes are straight, with a controllable pore size ranging from 25 to 65 nm, and have a barrier layer at their bottom.

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