

Influence of the electrolyte composition on formation process and morphology of anodic titanium oxide nanotubes

Ryota Kojima, Yasuo Kimura, and Michio Niwano

Laboratory for Nanoelectronics and Spintronics, Research Institute of Electrical Communication, Tohoku University 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
phone: +81-22-217-5502, fax: +81-22-217-5503
email: ykimura@riec.tohoku.ac.jp

Titanium oxide (TiO_2) nanotubes have attracted great interest because of its superior properties such as high photocatalytic activity and high biological affinity. Applications of TiO_2 nanotubes to solar cells, gas sensors and orthopedic implantation have been reported. Anodization of metal titanium (Ti) is a promising method to fabricate TiO_2 nanotubes, since it enables us to form a vertically-oriented TiO_2 nanotube film on a substrate[1,2]. When we apply TiO_2 nanotube films to devices, we need to control the structural properties of anodic TiO_2 nanotube films. The structural properties of nanotube films depend strongly on anodization conditions such as the composition of electrolyte and the anodic potential. Recently, it has been revealed that water dissolved in an organic electrolyte has significant effects on the shape of TiO_2 nanotubes[3]. However, its mechanism has not been fully understood. In this study, we have investigated the anodization process of a Ti film deposited on a Si crystal substrate covered with a thin silicon dioxide (SiO_2) layer. In order to fabricate well-ordered TiO_2 nanotube films, we explored in detail the influence of electrolyte composition on the anodization process of a Ti film.

A 1- μm thick SiO_2 layer was formed on a Si crystal substrate by wet thermal oxidation. A metal Ti film of 3 μm in thickness was deposited on the SiO_2 layer by the DC magnetron sputtering method. The Ti film was anodized in a solution cell made of polytetrafluoroethylene (PTFE) as shown in Fig. 1. Ethylene glycol solutions containing 0.05-0.3 M ammonium fluoride (NH_4F) and 1-10 vol% deionized water were prepared as an electrolyte. A platinum wire was used as a counter electrode to apply a constant anodic potential of 40 V to the Ti film. The TiO_2 nanotube films were characterized by a field-emission scanning electron microscope (FE-SEM).

Figure 2 shows morphology of anodic TiO_2 nanotube films formed by anodization in different electrolyte compositions. We indicate by a closed dashed line the region where well-ordered nanotube films were synthesized; outside the region, surface roughening and/or rib formation were observed. From Fig. 2, we can see that concentrations of both NH_4F and water in the electrolyte

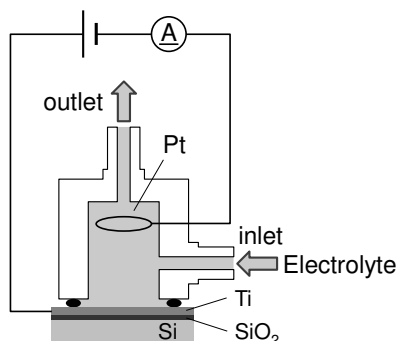


Fig. 1: Schematic of a solution cell.

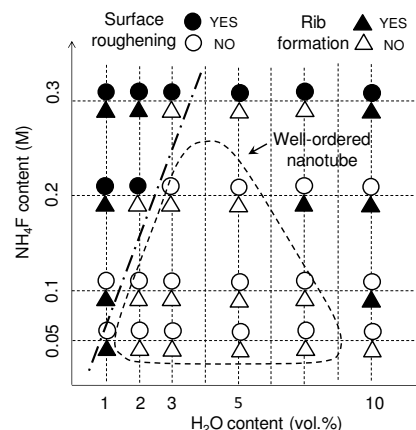


Fig. 2: Morphologies of anodic TiO_2 nanotube films formed by anodization in different electrolyte compositions.

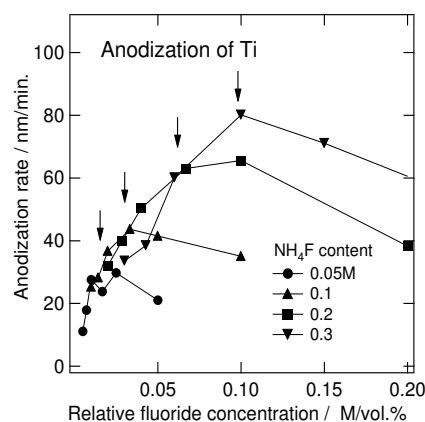


Fig. 3: Anodization rate of Ti plotted as a function of the relative fluoride concentration for different NH_4F concentrations. Arrows indicate the transition point.

influence the formation process of TiO_2 nanotube films. The anodization rate of Ti as a function of a ratio of fluoride concentration to water was shown in Fig. 3. We determined the anodization rate of a Ti film from the difference between the thicknesses of Ti films before and after incomplete anodization. It is evident in Fig. 3 that the anodization rate increases and then drops with increase of the relative fluoride concentration. These trends can be identified for all the fluoride concentrations, although the transition point (arrows in Fig. 3) at which the anodization rate begins to decrease depends on the fluoride concentration. In Fig. 2, we indicate by a dot-dashed line the boundary where the trend of anodization rate changed. On the left-hand side of this line, the anodization rate was reduced with increase of the relative fluoride concentration. This line also shows the boundary where the morphology of nanotube films changed. These indicate that the relative fluoride concentration in the electrolyte have significant effects on formation process and morphology of anodic TiO_2 nanotubes.

References

1. V. Zwilling, E. Darque-Ceretti, A. Boutry-Forveille, D. David, M. Y. Perrin and M. Aucouturier, *Surf. Interface Anal.* **27**, 629 (1999).
2. R. Kojima, Y. Kimura, and M. Niwano, *J. Electrochem. Soc.* **159**, D629 (2012).
3. A. Valota, D. J. LeClere, P. Skeldon, M. Curioni, T. Hashimoto, S. Berger, J. Kunze, P. Schmuki, and G.E. Thompson, *Electrochim. Acta* **54**, 4321 (2009).