## Structure Control of Mesoporous Anodic Crystalline TiO<sub>2</sub> Films by Changing Basicity of Hot Phosphate/glycerol Electrolytes

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Anodic TiO<sub>2</sub> nanotubular films have attracted much attention from the point of the view of applications such as photocatalysts, dye-sensitized solar cells (DSSCs), biomedical devices, electrochromic materials and so on. In most cases, such anodic  $\mathrm{TiO}_2$  nanotubular films are formed in the organic electrolytes containing fluorides and are amorphous structures just after anodizing. Therefore, post-annealing of the anodic specimens is indispensable for crystallization of TiO<sub>2</sub> nanotubes. Recently, various structured TiO<sub>2</sub> films such as branched tubes, double-walled tubes and bamboo can be formed by changing anodizing conditions. In addition, the chemical and physical properties of the anodic TiO<sub>2</sub> films are strongly affected by the nanostructure of them, suggesting that the control of the nano structures of the films is quite important to improve such properties for applications.

On the other hand, recently, we reported that the anatase crystalline  $TiO_2$  meso-porous film was formed by anodizing of a titanium specimen without annealing procedures [1,2]. In that report, the titanium specimen was anodized at 20 V in a hot phosphate/glycerol electrolyte at 433 K. The obtained films crystallized to anatase crystal and had mesoporous structures with pore diameters as small as ~10 nm, leading quite high surface areas. However, the obtained porous structure was disordering and it was difficult to control the structure without changing the crystallinity.

In this study, titanium specimens were anodized at 20 V in different basic electrolytes containing the mixture of  $K_3PO_4$ ,  $K_2HPO_4$  and  $KH_2PO_4$  at 433 K. We investigated the influence of basicity of the phosphate/glycerol electrolytes on crystallinity and mesoporous structures of anodic TiO<sub>2</sub> films.

The electropolished titanium specimens were anodized in glycerol electrolytes containing phosphates such as  $K_3PO_4$ ,  $K_2HPO_4$  and  $KH_2PO_4$  at 433 K under a nitrogen atmosphere. Total concentration of the phosphates was 0.8 mol dm<sup>-3</sup> and the details of the phosphate mixing ratio are shown in Table 1. The water content in the electrolyte was ~0.03 mass%. A platinum sheet was used as a counter electrode.

The crystallinity, morphologies and pore size of the anodic films were inspected with XRD, high resolution TEM, SEM and nitrogen gas adsorption/desorption isotherms. The pore size distribution was analyzed using BJH method, which is useful for mesopores in the range of 2–50 nm size.

**Table 1** Concentrations (mol dm<sup>-3</sup>) of the phosphate electrolytes used in anodizing.

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	P1	P2	P3	P4
K <sub>3</sub> PO <sub>4</sub>	0.6	0.4	0.2	-
$K_2HPO_4$	0.2	0.4	0.6	0.4
$KH_2PO_4$	-	-	-	0.4

From current transients of titanium during anodizing in the each hot phosphate/glycerol electrolytes at 20 V for

3.6 ks, the specimen anodized in higher basicity of electrolytes showed higher anodic current density. This result suggested that the higher basicity induced the formation of the anodic films or other oxidation reactions (for example, oxygen evolution).

From XRD patterns of the anodic films, the sharp peaks due to the presence of anatase crystalline TiO<sub>2</sub> appeared in the pattern of the all specimens, even though the film was not annealed after anodizing. In the case of all specimens, the 004 peak anatase TiO<sub>2</sub> is the strongest, whereas the most intense 101 peak for randomly oriented anatase is missing. In our previous report [1], the similar result was obtained in the P3 phosphate/glycerol electrolytes. In addition, from Scherrer's equation for the 004 peaks, the crystal grain size of the all specimens was about 10 nm. This result suggested that the orientation of the crystal grains and grain size were not affected by the basicity of the electrolytes during anodizing. From high resolution TEM of the TiO<sub>2</sub> films formed in P1 and P3 electrolytes, they are obvious that the nanocrystals are surrounded by amorphous matrix in both films. The crystal area of the films anodized in the P1 and P3 electrolytes were almost the same each other. These results suggested that the crystallinity of the obtained film was not affected by the basicity of the hot phosphate electrolyte during anodizing.

Fig. 1 shows cross-sectional SEM observations of the TiO<sub>2</sub> films anodized in P1 – P4 electrolytes for 3.6 ks. From the inset images in Fig. 1, the thickness of the P1, P2, P3 and P4 are 12.5, 9.6, 5.6 and 3.9  $\mu$ m. This result suggested that the higher basicity of the electrolytes accelerated the film formation rate during anodizing. The most interesting feature was that the porous structure was strongly affected by the basicity of the phosphate electrolytes. From Fig. 1, we can see that the porous structure became highly ordered cylindrical with increase basicity of the electrolytes.



**Fig. 1** Scanning electron micrographs of fractured cross-sections of the films anodized in (a) P1, (b) P2, (c) P3 and (d) P4 electrolytes for 3.6 ks. The insets are low magnification images of the cross-sections.

Reference

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