Fabrication of Self-Organized Titania Nanostructures on Glass by Combinational Anodizing Technology

S. Z. Chu, S. Inoue, K. Wada, and S. Hishita
Advanced Materials Lab., National Institute for Materials Science (NIMS)
Namiki 1-1, Tsukuba, Ibaraki, 305-0044, Japan

Introduction. Nanostructured TiO$_2$ materials are of considerable interest for many applications such as electronics, photocatalysis, optoelectronics, solar cells, chemical sensors, and energy storage systems. In previous studies, we had fabricated various TiO$_2$ nanomaterials in form of nanotubules, nanorods, and nanoporous films through a sol-gel method $^1$ or electrodeposition. $^2$ In the present study, we report the fabrication of versatile titania nanostructures (nanoporous films, integrated arrays of nanodots and nanocolumns) on glass substrates by a combinational anodizing technology.

Experimental. As starting specimens, a highly pure aluminum layer (99.999%, ~1.7 nm) and a highly pure titanium layer (99.99%, ~300 nm) were superimposedly deposited on a glass substrate (Corning 7031, 25 × 110 × 0.7 mm) by a RF-sputtering. The specimens were anodized successively in two steps. In the first step, the specimens were potentiostatically in phosphoric, oxalic, or sulfuric acid solutions down to the Ti/glass to obtain porous alumina films with different pore densities and dimensions. In the second step, the anodic alumina films were used as a porous electrical filter to perform a through-mask anodization over the underlying titanium layer on glass. Titanium anodization was performed in constant current mode or constant potential mode in different acidic solutions to obtain dense-type or porous type titania nanostructures. The morphologies of the resultant specimens were observed by FESEM with EDX. The chemical states of as-anodized titania films were analyzed by XPS. The crystallographic structures of specimens were analyzed by XRD and TEM. The transmittance spectra of the specimens were measured by a UV-Vis spectrometer.

Results and Discussion. Figure 1a shows an array of titania nanocolumns on Ti/glass formed by a combinational constant potential-constant current (CP-CC) anodization. The constant-potential anodization of aluminum layers down to the Ti/glass produced not only self-organized porous alumina films but also arrays of titania nanodots under the alumina nanopores, with the inherited patterns of the overlying anodic alumina films. In the successive constant-current anodization of titanium layers, the titania nanodots grew along the pores of anodic films due to the volume expansion, with the height proportional to anodizing potentials ended at last. Figure 1b shows a representative nanoporous titania film on glass, which was formed by a successive constant potential-constant potential (CP-CP) anodization in different electrolytes. The porous anodic titania film possesses uniform and parallel nanopores (~30 nm, ~90 nm interval) corresponding to the overlying alumina film, indicating a inductive effect of porous alumina film on the initiation and formation of porous titania film. As the titanium anodization was carried out completely down to the glass substrate, a transparent alumina/titania specimen with a transmittance of ~40% was achieved. The analysis results of the EDX analysis confirmed that the anodic titania films contained a certain amount of nitrogen, and the XPS analysis suggested that the titanium element of as-anodized specimens existed in titanium oxide (IV) and titanium nitride (III). TEM observation revealed that the as-anodized titania films were predominantly amorphous with numerous germainal crystals (5 – 10 nm across) embedded in the pore walls. The anodic titania films (~1 μm) are transparent (~40 %T) but exhibit relative high absorbance. Thermal heating at 600 °C transferred the porous titania films from amorphous into polycrystalline anatase, and leaded to a strong absorbance in UV light range with remaining transparent in visible light range.

Conclusions. Versatile anodic titania nanostructures, nanodots, nanocolumns, and nanoporous films with different pore or strut sizes (~20 – 100 nm) and intervals (50 – 450 nm), were successfully fabricated on glass by a combinational anodization for many applications.

References

![Fig.1 FESEM images of (a) surface morphology of a titania nanocolumn array and (b) fracture section of a nanoporous anodic titania film on glass after the removal of the overlying anodic alumina films.](image-url)