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

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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, 2] or electrodeposition.[3] 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 (99.99%, ~1.7 μm) 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 EDXA. 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 (~ϕ30 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 germinal 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 (ϕ20 ~100 nm) and intervals (50 ~ 450 nm), were successfully fabricated on glass by a combinational anodization for many applications.

References

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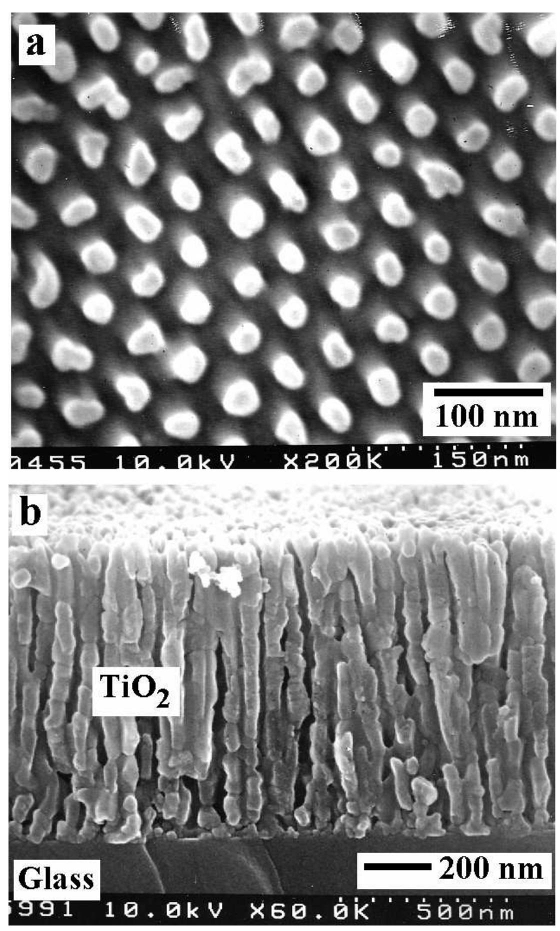

Fig.1 FESEM images of (a) surface morphology of a titania nanocolumn array and (b) fracture section of a nanoporous anodic titania film on glass after the removal of the overlying anodic alumina films.