AAO-assisted synthesis of highly ordered, large-scale TiO$_2$ nanowire arrays via sputtering and atomic layer deposition

Zhao Yao, Cong Wang, Yang Li and Nam-Young Kim

Abstract

Highly ordered nanoporous anodic aluminum oxide (AAO) thin films were fabricated in oxalic acid under a constant voltage via a two-step anodization process. To investigate the high-aspect-ratio (7.5:1) filling process, both sputtering and atomic layer deposition (ALD) were used to form TiO$_2$ nanowires. Field emission scanning electron microscopy and high-resolution transmission electron microscopy images indicated that mushroom-like TiO$_2$ structures were sputtered onto the AAO template surface, and the ALD-coated TiO$_2$ exhibited fine filling results and clear crystal grain boundaries. Large-scale and free-standing TiO$_2$ nanowire arrays were liberated by selectively removing the aluminum substrate and AAO template via a wet etching process with no collapsing or agglomeration after the drying process. ALD-deposited TiO$_2$ nanowire arrays that were 67 nm in diameter and 400 nm high were transferred from the AAO template. The ALD process enabled the rapid, simple synthesis of highly ordered TiO$_2$ nanowire arrays with desired parameters such as diameter, density, and thickness determined using diverse AAO templates.

Keywords: Titanium oxide; Nanowire arrays; Anodic aluminum oxide; Atomic layer deposition

Background

One-dimensional TiO$_2$ thin films with nanoscale structures, such as nanotubes, nanorods, and nanowires, present a variety of applications, including catalysis [1-3], gas sensing [4,5], and energy harvesting [6,7], due to their large surface-to-volume ratio, convenient band gap, and quantum confinement effects. Research into synthesizing TiO$_2$ materials with nanoscale structures has significantly increased in recent years. Areas of focus include hydrothermal methods [8,9], pulsed laser deposition (PLD) [10], and the anodization of titanium films [11,12]. In addition, an easily controlled template-assisted growth method has also drawn significant interest because the template can be used to directly form a desired nanostructure. Using a template with a specified shape, diameter, density, and arrangement allows a large number of desired targets to be duplicated once the specific template structure has been formed. Even large-scale films can be easily prepared via a template synthesis. Various materials such as lithographed polymers [13], natural materials [14], and anodized metals (e.g., Al, Ti, and Mg), many of which are abundantly available, can be used for the template [11-16]. AAO thin films prepared via the two-step anodization of Al have a highly ordered honeycomb porous structure, and their preparation is more easily controlled than other materials. Compared to other strategies, this method is a simple, fast way to grow patterned nanostructure.

In AAO-assisted synthesis of nanostructures, sol–gel and electrochemical deposition are both well-known liquid-phase deposition methods for forming TiO$_2$ nanowires [17,18]; however, both methods require drying and sintering processes to promote crystallinity. During the sintering process, the templates are fired, which complicates their removal. While AAO templates are removed using acid or alkaline solutions, the nanowire or nanotube arrays would most likely agglomerate, which may destroy their regular, vertical alignment [17]. In contrast, physical vapor deposition (PVD) processes can synthesize single-crystalline structures; however, the pattern size is usually limited by the template or photoresist aspect ratio due to self-limiting step coverage. An aspect ratio above 5:1 is generally not

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attainable using e-beam evaporation and sputtering system. Therefore, either the nanostructure size or height is limited by the PVD process. Consequently, vapor-phase deposition via chemical vapor deposition (CVD) or ALD exhibits potential for synthesizing nanowires or nanorods because it is not subject to such aspect ratio constraints. Combining ALD with AAO templates is the most promising strategy for synthesizing nanostructures. However, in previous researches [1,17,19], it shows difficulty to prevent the nanowires from agglomeration after a wet etching process. Otherwise, the height of the nanowires is limited to approximately 100 nm [13,20].

In this study, ALD was compared to PVD as a step coverage problem by filling 500-nm-thick nanoporous AAO thin films with 67-nm-diameter pores as templates for the TiO$_2$ nanowires. The sputtering and ALD deposition rates were reduced to suit this high-aspect ratio. After the TiO$_2$ deposition, the surface and cross-sectional structures of the TiO$_2$ and Al$_2$O$_3$ mixtures were investigated via field emission scanning electron microscopy (FE-SEM) and elemental mapping, and the interface between the AAO and TiO$_2$ were characterized via X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HR-TEM). After the TiO$_2$ nanowire arrays liberated from AAO templates and transferred onto Si substrate, highly ordered, large-scale, and vertically aligned nanostructures were achieved without agglomeration.

Methods

The nanoporous AAO templates were fabricated via a prototypical two-step anodization electrochemical method using high-purity (99.999%) aluminum foil in a 0.3 M oxalic acid electrolyte at a temperature of 0.2℃ under a constant anodization voltage of 40 V for 10 min. Next, a 500-nm-thick fine, self-ordered, hexagonal, nanoporous structure formed on the aluminum foil surface as a patterned template for nanorods, nanotubes, or nanowires. TiO$_2$ thin films were deposited onto the nanoporous template via sputtering (SPS 4150, UL-TECH, Daegu, Korea) and ALD (TFS 200, BEN-EQ, Vantaa, Finland). For the sputtering process, the sputtering power, Ar flow rate, and chamber pressure were 2 kW, 80 sccm, and 4e− 6 Torr, respectively. During the ALD process, single-crystalline TiO$_2$ thin films were grown at 200℃ and 230 mTorr using TiCl$_4$ and H$_2$O as the precursor vapors. During the growth process, the TiCl$_4$ and H$_2$O were delivered to the chamber using an N$_2$ carrier gas at a flow rate of 50 sccm. The pulse time, purge time, and deposition rate were 250 ms, 1 s, and 0.05 nm/cycle, respectively. Moreover, top and cross-sectional views of the original and TiO$_2$-coated nanoporous AAO thin films were observed via FE-SEM (Hitachi S-4800, Hitachi, Ltd., Chiyoda, Tokyo, Japan). The crystal structure was investigated via XRD (D/MAX-2500 V/PC, Tokyo, Japan) using Cu Kα radiation (λ = 0.154 nm) and a sampling width of 0.02° with a scan speed of 4’/min. Finally, HR-TEM (JEM 2100 F, JEOL Ltd., Akishima, Tokyo, Japan) was used to confirm the crystal structure of the as-deposited TiO$_2$ thin films and filling process. The aluminum substrate was then completely removed using a saturated CuSO$_4$ solution with a small amount of HCl (38 wt%), and the AAO template was etched in 6 wt% H$_3$PO$_4$ for 20 h at 23℃ as shown in Figure 1a. To avoid any surface tension that may destroy the nanostructures, all samples were dried at room temperature for 12 h without annealing.

Results and discussion

Figure 1a shows the schematic process for fabricating the free-standing TiO$_2$ nanowire arrays. A 2 cm × 2 cm AAO template was prepared via the two-step anodization shown in Figure 1b. The samples fabricated by filling the AAO templates with TiO$_2$ via sputtering or ALD are shown in Figure 1c. The surface color for the ALD-coated AAO template changed, while the sputtered AAO template remained unchanged. This macroscopic phenomenon primarily resulted from the multilayer interference effect [21], which also indicated that the ALD-coated TiO$_2$ yielded better filling than the sputtering process. Finally, TiO$_2$ nanowire arrays were fabricated via ALD by separately removing the aluminum substrate and AAO template via wet etching. In addition, the surface morphology of the fabricated nanowire arrays were characterized by SEM as shown in Figure 1d, which indicates highly ordered, large-scale, and free-standing TiO$_2$ nanowire arrays.

Figure 2a,d shows the cross-sectional and top SEM images for a 500-nm-thick nanoporous AAO thin film with a 67-nm pore diameter and approximately 10$^{10}$ cm$^{-2}$ pore density. Figure 2a shows well-ordered cylindrical pores with a high aspect ratio which were observed after the two-step anodization. All of the pores run straight from top to bottom, which confirms that the nanoporous AAO template can be used to pattern both nanotubes and nanowires. In addition, the oxalic acid electrolyte dissolved parts of the AAO surface to form small, terminated pores [22], which appear as twinned pores (Figure 1d). Despite research into the cause of twinned pores being unclear, such a nanostructure would convert into an ideal hexagon with increased anodization time [23,24]. Figure 2b,e shows mushroom-like TiO$_2$ thin films coated by sputtering onto AAO membranes. Due to the self-limited growth mechanism and high aspect ratio (7.5:1), most of the TiO$_2$ films were concentrated on the surface of the AAO film surface. Increasing the deposition time decreased the nanopore diameter until they ultimately closed. However, the templates are well filled via ALD as shown in Figure 2c. Clear crystal grain boundaries were observed in Figure 2f, and there were no pinholes in the template surfaces.
To examine the TiO$_2$ and AAO template interface and TiO$_2$ thin film crystallinity, TiO$_2$ nanowire arrays grown on the AAO membrane via ALD were analyzed by XRD and HR-TEM. The XRD profile for the AAO-assisted TiO$_2$ synthesis is shown in Figure 3. A narrow, strong reflection peak from the (101) plane was identified at 2$\theta$ = 25.4°. Reflection peaks for the (103), (200), (105), (211), and (204) planes were also observed; however, their intensities were significantly weaker than the main (101) plane peak, which indicates that the ALD-coated TiO$_2$ nanowires contained a pure anatase phase (JCP-DS No. 21–1272) with a mostly (101) orientation. The Al substrate peaks appeared in Figure 3 at 22.36°, 38°, 64°, 44.78°, and 65.18°; however, the AAO membrane peaks were absent. This finding may result from the AAO thin films not being annealed (higher than 200°C) during processing; the Al$_2$O$_3$ should be amorphous after the two-step anodization.

The TEM sample was prepared using a focused ion beam (FIB) as shown in Figure 4a. Because of the aluminum

Figure 1 Processes for fabricating highly ordered, large-scale TiO$_2$ nanowire arrays. (a) Schematic diagrams of the process to produce the nanowire arrays, (b) photograph of a 2 cm × 2 cm AAO template, (c) top view of the AAO templates after coating TiO$_2$ via (i) sputtering and (ii) ALD with a mean pore diameter of 67 nm, and (d) top and cross-sectional SEM images of the highly uniform and free-standing TiO$_2$ nanowire arrays.

Figure 2 FE-SEM images of 500-nm-thick nanoporous AAO thin film on the aluminum substrate. (a) Cross-sectional results before and after TiO$_2$ filling by (b) sputtering and (c) ALD, and (d) the surface results before and after TiO$_2$ filling by (e) sputtering and (f) ALD.
anodization mechanism [25,26], a viable 21.5-nm-thick barrier layer was created, as marked in Figure 4b. Accordingly, U-shaped TiO$_2$ nanowires were observed after the ALD process. The TiO$_2$ and Al$_2$O$_3$ nanowire arrays were confirmed via energy-dispersive X-ray spectrometer (EDS) mapping, which illuminated Ti and Al distribution. Figure 4c marks the EDS detection area with the yellow line, and all of the element distribution profiles are given in Figure 4c-1,c-2,c-3, which proved that both the Al and Ti concentrations periodically changed along the horizontal axis. In Figure 4c-2,c-3, the change in Al precisely exhibited an opposite tendency to the Ti across the entirety of the AAO arrays and TiO$_2$ nanowires. The AAO nanopores were fully filled by the ALD process based on the cross-sectional structure and EDX spectroscopic image.

To verify the above findings, TEM images of the AAO arrays and TiO$_2$ nanowires were collected and are shown in Figure 5. Both the U-shaped TiO$_2$ nanowire ends and bottom barrier layer were observed in the low-magnification TEM images (Figure 5a). The HR-TEM images of the TiO$_2$ and Al$_2$O$_3$ interface and barrier layer were used to examine the crystal facets. The HR-TEM image in Figure 5b directly shows single-crystal anatase TiO$_2$. Two confirmed lattice fringes were present with a distance of 0.35 and 0.47 nm, which corresponded to the {101} and {002} facets shown in the fast Fourier transformation (FFT) patterns (Figure 5d) in region 1 [27], respectively. Figure 5c shows the HR-TEM image for the AAO barrier layer and Al substrate. A 0.2-nm lattice fringe appeared in region 3, which corresponded to the {200} Al crystalline plane in the FFT patterns (Figure 5f) of region 3. However, crystalline Al$_2$O$_3$ was found in neither the HR-TEM images nor the FFT patterns as shown in region 2 and Figure 5e, respectively. These findings all agree with the XRD results.
Figure 5 TEM images of the AAO template coated with TiO$_2$ using ALD. (a) Cross-section of the TEM samples. (b, c) HR-TEM images of the anatase TiO$_2$ (region 1), AAO (region 2), and Al substrate (region 3). (d-f) The FFT patterns for regions 1, 2, and 3, respectively.

Figure 6 SEM images of the transferred TiO$_2$ nanowires. The (a, b) top and (c, d) cross-sectional views of 400-nm-high free-standing TiO$_2$ nanowire arrays with a diameter of 66.8 nm.
Finally, 400-nm-tall highly crystalline anatase TiO$_2$ free-standing cylindrical nanowire arrays 67 nm in diameter formed using the AAO template via ALD as shown in Figure 6. The non-edge parts of the nanowire arrays were vertically arranged highly ordered TiO$_2$ nanowires with uniform diameters. Only a few small nanowires are shown in the enlarged SEM image (Figure 6b) due to the twinned pores observed in Figure 2d. However, the cross-sectional images from the sample edge (Figure 6c,d) contain some anomalous nanowires. Notably, the two nanowires marked by the white circle in Figure 6d were amalgamate with each other at the top, which may be due to damage during the drying and transfer processes.

Conclusions

In this study, self-ordered nanoporous AAO thin films with high aspect ratios and smooth sidewalls were successfully prepared via the two-step anodization of aluminum foil. The AAO thin film template was coated with a TiO$_2$ layer via sputtering and ALD. The sputtered TiO$_2$ layer formed a mushroom-like structure on the AAO template surface, which may form pinholes within the AAO nanorods. In contrast, the nanoporous AAO thin films were satisfactorily filled with TiO$_2$ via the ALD approach. Furthermore, the ALD process promoted the crystallization of the as-deposited TiO$_2$ films to form a single anatase TiO$_2$ crystal with a low index of (101) and (002). Based on these findings, combining the ALD approach with a wet etching process yielded highly ordered, large-scale, and free-standing TiO$_2$ nanowire arrays with potential applications to be explored in further work, such as sensing, catalysis, and energy applications.

Competing interests

The authors declare that they have no competing interests.

Authors’ contributions

ZY conceived of this study, managed the whole study, and drafted the manuscript. YL and CW carried out the fabrication and measurement. As the corresponding author, N-YK managed the main conception, guided the research, and revised the manuscript. All authors read and approved the final manuscript.

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