Growth Mechanism of TiO₂ Nanotube Arrays in Nanopores of Anodic Aluminum Oxide on Si Substrates by Atomic Layer Deposition

Chien-Min Liu,a Chih Chen,a,z and Hsyi-En Chengb

1Department of Materials Science and Engineering, National Chiao-Tung University, Hsinchu 30010, Taiwan
2Department of Electro-Optical Engineering, Southern Taiwan University, Tainan 710, Taiwan
3Department of Electro-Optical Engineering, Southern Taiwan University, Tainan 710, Taiwan

In this study, we combined atomic layer deposition and anodic aluminum oxide (AAO) on a silicon substrate and developed self-aligned TiO₂ nanotube arrays. We studied the growth mechanism of TiO₂ nanotubes on the inner wall of AAO at 100 and 400°C. We found that at 100°C TiO₂ grew in a layer-by-layer manner. Therefore, it can be grown into TiO₂ nanotube arrays with very thin walls. However, at 400°C TiO₂ needs to first form a 2.5-nm amorphous layer, before becoming crystalline TiO₂ via a phase transformation, and growing into crystalline TiO₂ nanotube arrays along the preferred plane (101) by means of a space-limited growth mechanism.

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Because TiO₂ nanotubes have a large surface-to-volume ratio, they have been extensively studied and applied to photocatalysis,5,6 sensors,7,8 and dye-sensitized solar cells.9 In all these applications, the surface area of the TiO₂ nanotubes is an important factor that determines the efficiency and performance. In terms of the structure of nanotubes, for a given length, the thinner the wall thickness, the larger the surface area per unit volume. Larger surface areas can increase the liquid contacting area of TiO₂ and subsequently improve its performance in photocatalytic applications. In addition, a larger nanotube surface area in dye-sensitized solar cells can increase the contact area between the nanotube and the dye. For a fixed diameter, the thinner the wall thickness, the larger the relative nanotube inner space. A larger space may increase the dye-filling of nanotubes in dye-sensitized solar cells. These two changes can effectively improve the TiO₂ nanotube performance in dye-sensitized solar cells. Therefore, developing TiO₂ nanotubes with thin walls to increase their performance is an important research focus. Furthermore, modern component manufacturing mostly uses Si as a substrate, therefore, whether or not the manufacturing process can be integrated with a Si substrate is also an important issue to be considered.

Current studies of TiO₂ nanotube growth are mostly done through the anodization of a Ti foil anode.10-12 Although this method fabricates very neatly aligned TiO₂ arrays, the wall thickness cannot be controlled for very thin samples, and the array cannot be integrated with a Si substrate.

Atomic layer deposition (ALD) is a deposition technique in which the film thickness can be precisely controlled and of which the step coverage is excellent,14,15 because its coating method is under surface reaction control. Anodic aluminum oxide (AAO) is a highly regular template material for which the manufacturing process can be easily integrated with various substrates.21-23 Therefore, if these two techniques can be combined, regularly arrayed thin-walled TiO₂ nanotube arrays can be grown on a Si substrate, and this method has been published elsewhere.24,25 However, these studies have not systematically investigated the mechanism of TiO₂ growth on an AAO wall, particularly the mechanism of TiO₂ nucleation. Meanwhile, studies of growth mechanisms at different temperatures are also lacking.

In this study, we used AAO and ALD to fabricate TiO₂ nanotube arrays with different numbers of deposition cycles on a Si substrate. Using transmission electron microscopy (TEM), we observed TiO₂ nucleation and growth on AAO walls at different growth temperatures. Moreover, because TiO₂ is deposited on a SiO₂ surface at the bottom of AAO nanopores, we also studied the growth mechanism of TiO₂ on a SiO₂ surface.

Experimental

In our experiment, we used a thermal evaporation system to directly deposit a 1-μm aluminum film on a 4-in. P-type (100) Si substrate under high vacuum (< 4 × 10⁻⁶ Torr), which became the anodic aluminum oxide. The purity of the aluminum ingot used in this study was 99.999%. With aluminum film as the anode, inert metallic platinum (Pt) as the cathode and 0.3 M oxalic acid (H₂C₂O₄) as the electrolyte, we fabricated nanopore arrays of high regularity using a two-step anodization process under 40 V bias voltage. As shown in Fig. 1a, the newly fabricated AAO had an average diameter of 70 nm and an average pitch of 100 nm. We then used ALD to deposit TiO₂ onto the AAO nanostructures. In the experiment, TiCl₄ was used as the precursor and deionized water as the reactant to deposit TiO₂ onto the AAO. During deposition, the operating pressure in the reaction chamber was maintained at 5 Torr, with the deposition temperatures being 400 or 100°C and the deposition cycle numbers being 100, 200, 300, and 700. TiCl₄ was added for 1 s, followed by TiCl₄ washing for 10 s; H₂O was then added for 1 s, and the samples were cleaned in H₂O for 10 s. With these process parameters, we obtained high quality TiO₂ nanotubes. After the deposition was completed, TiO₂ would cover the AAO nanopore surface as a thin film, as shown in Fig. 1b. This deposition was followed by polishing to successfully remove the TiO₂ covering the AAO surface, as shown in Fig. 1c. Finally, the specimen was soaked in 0.1 wt % NaOH(aq) solution to remove AAO, to obtain TiO₂ nanotube arrays that were vertically aligned on the Si substrate, as shown in Fig. 1d. Subsequently, the nanostructure and nucleation-growth mechanism of TiO₂ nanotubes formed under different temperatures were analyzed by TEM. To observe the ALD TiO₂ growth mechanism on AAO and SiO₂ surfaces, AAO was not removed for TEM analysis (Fig. 1e).

Results and Discussion

Through controlling the ALD deposition cycle number, we can accurately control the wall thickness of nanotubes, whereas through controlling the deposition temperature, the growing TiO₂ crystal structure can be controlled. Figures 2a-2e and 2d and 2f show the plane-view TEM images from 100, 300, and 700 cycles at 100°C, and 200, 300, and 700 cycles at 400°C, respectively. From the imaging results, we can see that the respective wall thicknesses of the samples grown at 100°C-100 cycles and 400°C-200 cycles were 6.6 and 10.6 nm, respectively. When the deposition cycle number was

E-mail: chih@cc.nctu.edu.tw
are deposited using ALD; the TiO2 layer is removed from the top surface; self-aligned TiO2 nanotube arrays after the removal of AAO.

Figure 1. (Color online) Illustration of the production process of TiO2 nanotube arrays: (a) AAO is produced on a Si substrate; (b) TiO2 nanotube arrays are deposited using ALD; (c) the TiO2 layer is removed from the top surface; (d) self-aligned TiO2 nanotube arrays after the removal of AAO.

increased to 300 cycles, the respective wall thicknesses at 100 and 400°C were 26.6 and 17.3 nm, respectively. Using the correlation between cycle number and wall thickness, we calculated the deposition rates at 100 and 400°C to be 0.1 and 0.067 nm per cycle, respectively. When the deposition cycle number was increased to 700 cycles, the wall thicknesses estimated from the growth rate results were 70 and 46.9 nm at 100 and 400°C, respectively. This may be because the precursors are not able to diffuse into the nanopores with few nanometers in diameter, as shown in Figs. 2c and 2f. Comparing the surface of the inner wall at 100 and 400°C, we found that the surface of the inner wall at 100°C was very smooth, whereas the surface of the inner wall at 400°C was rather rough. In addition, the comparison of the growth rates at 100 and 400°C showed that the growth rate at 100°C was higher than that at 400°C. The differences observed in the wall surface and growth rate were related to the differences in the growth mechanisms at the two temperatures, which will be discussed in detail later in this paper.

The nanopore dimension of the AAO template used in this study was 70 nm. Therefore, from the estimated wall thickness we anticipated that the TiO2 should have grown into a nanorod structure after 700 cycles. However, from the results shown in Fig. 2c and 2f, we found that at 100°C-700 cycles and 400°C-700 cycles, TiO2 still formed nanotube structures with wall thicknesses of 32 and 33.5 nm, respectively. This may be because the precursors are not able to diffuse into the nanopores with few nanometers in diameter, as shown in Figs. 2c and 2f. Comparing the surface of the inner wall at 100 and 400°C, we found that the surface of the inner wall at 100°C was very smooth, whereas the surface of the inner wall at 400°C was rather rough. In addition, the comparison of the growth rates at 100 and 400°C showed that the growth rate at 100°C was higher than that at 400°C. The differences observed in the wall thicknesses at 100 and 400°C, respectively. The wall surface was very smooth at 100°C-700 cycles. Moreover, from the contrast of the TEM images we speculated that at 100°C the TiO2 deposition would be in an amorphous structure, which will be verified in a later section. The wall surface of 400°C-700 cycles was very rough, and the image contrast clearly showed polycrystalline structures of TiO2 deposited at 400°C. From these results, we concluded that we can precisely control both the wall thickness and nanostructure of our nanotubes by adjusting the cycle number and temperature during ALD deposition.

To further investigate TiO2 filling the AAO nanopores, we analyzed the cross-sectional TEM images. Figures 3a and 3b show the cross-sectional TEM images from 700 deposition cycles at 100 and 400°C, respectively. The wall surface was very smooth at 100°C-700 cycles. Moreover, from the contrast of the TEM images we speculated that at 100°C the TiO2 deposition would be in an amorphous structure, which will be verified in a later section. The wall surface of 400°C-700 cycles was very rough, and the image contrast clearly showed polycrystalline structures of TiO2 deposited at 400°C. From these results, we concluded that we can precisely control both the wall thickness and nanostructure of our nanotubes by adjusting the cycle number and temperature during ALD deposition.

To analyze the deposition of nanotube structures at 100 and 400°C, we utilized high-resolution transmission electron microscopy (HRTEM), select area diffraction (SAD), and x-ray photoelectron spectroscopy (XPS) in this study. Figure 4a shows the HRTEM image of 100°C-700 cycles, in which the amorphous structure can be observed. The inset image was from SAD of nanotubes that showed diffuse rings and confirmed the amorphous structure of the nanotube deposition at 100°C. Because the phase of an amorphous structure cannot be determined by SAD, we used XPS to conduct phase analysis in this study. Figure 4b is the XPS image of the 100°C-700 cycle experiment. From the image, we found that the peak position of Ti(2p) was at 458.8 eV. A comparison to the XPS database confirmed that the deposited nanotube phase at 100°C was TiO2. Figure 5a is the SAD pattern for the nanotubes formed at 100°C-700 cycles. The SAD pattern appeared as dotlike diffraction rings, suggesting that the nanotubes deposited at 400°C were in a polycrystalline structure. Diffraction rings were indexed as (101), (004), (200), (105), and (213). After comparing with JCPDS (no. 21-1272), we concluded that the nanotubes deposited at 400°C were the TiO2 anatase phase. Figure 5b is the HRTEM image of nano-

Figure 2. TEM plane-view images of TiO2 nanotube arrays at (a) 100°C-100 cycles, (b) 100°C-300 cycles, (c) 100°C-700 cycles, (d) 400°C-200 cycles, (e) 400°C-300 cycles, and (f) 400°C-700 cycles.

Figure 3. TEM cross-sectional images of TiO2 nanotube arrays at (a) 100°C-700 cycles and (b) 400°C-700 cycles.

Figure 4a shows the HRTEM image of 100°C-700 cycles, in which the amorphous structure can be observed. The inset image was from SAD of nanotubes that showed diffuse rings and confirmed the amorphous structure of the nanotube deposition at 100°C. Because the phase of an amorphous structure cannot be determined by SAD, we used XPS to conduct phase analysis in this study. Figure 4b is the XPS image of the 100°C-700 cycle experiment. From the image, we found that the peak position of Ti(2p) was at 458.8 eV. A comparison to the XPS database confirmed that the deposited nanotube phase at 100°C was TiO2. Figure 5a is the SAD pattern for the nanotubes formed at 400°C-700 cycles. The SAD pattern appeared as dotlike diffraction rings, suggesting that the nanotubes deposited at 400°C were in a polycrystalline structure. Diffraction rings were indexed as (101), (004), (200), (105), and (213). After comparing with JCPDS (no. 21-1272), we concluded that the nanotubes deposited at 400°C were the TiO2 anatase phase. Figure 5b is the HRTEM image of nano-
tubes using 700 cycles at 400°C. From the image, a polycrystalline structure can be observed. The inset image is the enlarged image of the dotted square, in which the lattice spacing in the two groups of planes was 3.52 and 2.378 Å, respectively. They were indexed as the (101) and (004) planes of the TiO$_2$ anatase phase.

From the above results and analyses, we discovered different growth rates and different surface morphologies at different temperatures. We speculated that the growth mechanism was the major factor affecting growth rate and surface morphology. Therefore, to understand the growth mechanisms at 100 and 400°C, we observed the nanostructure of the 100-cycle deposition by TEM. Figure 6a shows the cross-sectional TEM image of the 100°C-100 cycle nanotubes. From the image, we can see that TiO$_2$ on the side wall grew on the AAO surface but TiO$_2$ at the bottom grew on the SiO$_2$ surface. The wall thicknesses on the side wall and bottom were approximately the same and the inner wall surfaces of both coatings were very smooth, with a wall thickness of 6.6 nm. Figure 6b is the HRTEM image of the rectangular region of Fig. 6a. Our observations found that a 2.5-nm layer of SiO$_2$ existed between the Si substrate and the TiO$_2$, which means that in this study, TiO$_2$ was deposited onto two different surfaces, AAO and SiO$_2$. From the results of Fig. 6b, we found that TiO$_2$ on two different surfaces (AAO and SiO$_2$) contained the same wall thickness and the same amorphous structure. Therefore, at 100°C the growth thickness of ALD TiO$_2$ was not related to the surface. This kind of growth mechanism was denoted as layer-by-layer growth.
However, the growth mechanism at 400°C is different from that at 100°C. Figure 7 is the cross-sectional TEM image of the sample at 400°C-100 cycles. The results in this figure showed that TiO₂ had different surface morphologies on the AAO and SiO₂ surfaces. The TiO₂ on the SiO₂ surface was a continuous thin film, but the TiO₂ on the AAO surface had two different surface morphologies, with one being a continuous thin film as shown in region B and the other one being conical crystals dispersed in the continuous thin film as shown in region C.

To understand the growth mechanism of ALD TiO₂ on the two different surfaces (SiO₂ and AAO) at 400°C, we analyzed the TiO₂ nanostructures by HRTEM within the three rectangular regions labeled in Fig. 7. Figures 8a-8c are the HRTEM images of regions A, B, and C, respectively. Figure 8a shows that the TiO₂ continuous thin film on SiO₂ was composed of faced grains, with the thickness of the thin film equal to the grain size, which was 5–6.5 nm. Careful analysis of the face grain showed that it consisted of specific [101] planes. The reason for [101] plane formation was the relatively low enthalpy in this plane of TiO₂. From the above analysis, we deduced the growth mechanism of ALD TiO₂ on the SiO₂ surface. At the initial deposition cycle, TiO₂ first nucleated on the SiO₂ surface. Along with the gradual increase of the deposition cycle number, grains grew on the [101] plane of the nucleus. In addition, we found two different TiO₂ nanostructures on parts of the AAO surface. Figure 8b is the HRTEM image of region B. From the white dashed line labeled in the image, we can see that the TiO₂ continuous thin film on the AAO surface was an amorphous structure, with a thickness of 2.5 nm. Moreover, from the image we also found the existence of crystalline TiO₂ as shown with the white dashed circle. Therefore, we speculated that in the initial deposition cycles, ALD TiO₂ first formed an amorphous layer on the AAO surface, and then formed a crystalline TiO₂ nucleus inside the amorphous layer. Figure 8c is the HRTEM image of the conical crystal. From the image, we can see that this conical crystal was a single grain and that it was composed of an orderly stacking of [101] planes. Therefore, we concluded that after the formation of the TiO₂ nucleus, with the increase in deposition cycle number, the crystal had grain growth along the [101] plane.

To further understand the growth mechanism after the TiO₂ nucleation on the AAO surface at 400°C, we used TEM bright field (BF) and dark field (DF) imaging to observe the 300- and 700-cycle deposition at 400°C. Figures 9a and 9b are the respective plane-view TEM BF and DF images of 300 cycles. Figures 9c and 9d are the respective plane-view TEM BF image and DF image of 700 cycles. Figure 9a shows that the wall thickness at 300 deposition cycles was 17.3 nm. Compared to the DF image in Fig. 9b, we found that the wall thickness equaled the grain size in the orientation of the wall thickness. When the deposition cycle number was increased to 700 cycles, the wall thickness was 35 nm. Compared to the DF image in Fig. 9d, we found that the grain appeared to be in

Figure 6. TiO₂ nanotube arrays 100°C-100 cycles: (a) TEM cross-sectional image and (b) HRTEM image for the dotted rectangular area in Fig. (a).

Figure 7. TEM cross-sectional image of 400°C-100 cycle TiO₂ nanotube arrays. The crystalline TiO₂ layer is continuous on the SiO₂ surface, but it is not on the AAO surface.
the shape of a long cylinder, with the grain size equal to the wall thickness and the grain width shrinking toward the center part of the nanotube.

From the above results, we proposed a schematic diagram of the TiO$_2$ growth mechanism in the AAO nanopores at 400°C, as shown in Fig. 10. At the deposition initiation stage, TiO$_2$ formed an amorphous thin film on the AAO surface, as shown in Fig. 10a. When the deposition cycle number gradually increased, part of the amorphous thin film was transformed into a nucleus of anatase phase TiO$_2$. When the cycle number continued to increase, the nucleus continued to stack along the $[101]$ plane and grew into a conical grain, as shown in Fig. 10b. With the continuous increase in deposition cycles, the conical grain gradually grew, mainly along the nanotube circumferential direction. When the growth reached a certain size, such a grain contacts adjacent grains and subsequent horizontal growth is restricted. Therefore, it grew into a long cylindrical grain.
as shown in Fig. 10c. At this point, the deposition cycle number continued to increase, whereas the growth direction of the cylindrical grain was limited by the adjacent grains. Thus, the grain directed its growth toward the wall thickness of the nanotube. When the growth was close to the nanotube center, the space limitation caused the cylindrical grain to gradually decrease its grain size near the axis of the cylinder. Finally, it became a grain in a shape of a long cylinder with a cone at the top, as shown in Fig. 10d. From these results, we understood that the space in the AAO nanopores limited the growth pattern. Therefore, at 400°C, the nucleation needed high activation energy, thus the adjacent grains could not form a continuous thin film on the surface of AAO, whereas at 400°C, the nucleation could proceed and a polycrystalline structure could be formed. Therefore, at 400°C, the growth rate was lower than that at 100°C, whose growth mechanism was layer-by-layer growth. Therefore, at 400°C, the grain growth pattern was close to the nanotube center, the space limitation caused the growth pattern to be space-limited growth.

The results in Fig. 2 showed that the growth rate at 400°C was lower than that at 100°C. We found that the growth rates of the two temperatures were directly related to their growth mechanisms. At 400°C, the TiO2 deposition onto the AAO surface needed to form an initial amorphous layer and then underwent a process of phase transformation, nucleation, and growth. Therefore, during the grain growing process, only when the grain growth came into contact with the adjacent grains could continuous thin film be formed. Because of this, at 400°C, the nucleation needed high activation energy, thus the growth rate was lower than that at 100°C, whose growth mechanism was layer-by-layer growth. Therefore, at 100°C-100 cycles a continuous layer of TiO2 nanotubes cannot be formed, as shown in Fig. 6a, whereas at 400°C-100 cycles, a continuous crystalline layer of TiO2 nanotubes cannot be formed on the AAO surface, as shown in Fig. 7.

Conclusion

In the current research, after the integration of ALD and AAO technologies, self-aligned TiO2 nanotube arrays were generated on a Si substrate. By changing the temperature during the processing and controlling the number of deposition cycles, TiO2 nanotube arrays of varying wall thickness with amorphous structures (100°C) and polycrystalline structures (400°C) were produced. The growth mechanism at 100°C is layer-by-layer growth; the growth mechanism at this temperature is not related to the surface. The growth mechanism at 400°C is directly related to surface. After TiO2 forms an amorphous continuous thin film on the surface of AAO, phase transformation happens within the amorphous thin film forming a crystalline nucleus. Then the nucleus grows along the [101] plane grain. Finally, due to the space limitations, a column-shaped grain with a conical tip is formed.

References