Fabrication of Porous Al₂O₃ and TiO₂ Thin film hybrid composite using Atomic Layer Deposition and Properties Study

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Keywords: Atomic Layer Deposition (ALD), Anodic Aluminum Oxide (AAO), Porous TiO₂, Nano Tubular Structure

Abstract. Atomic layer deposition (ALD) has been used in advanced applications where thin layers of materials with precise thickness down to the nanometer scale are needed. Using anodic oxidation, we prepared the porous alumina. Anodic oxidation was carried out in 5°C 0.3M oxalic acid with anodizing voltages (~ 40 V) and two step anodization method. SEM shows that, these porous anodic oxides are well aligned and organized into high-density uniform arrays. Afterward, titanium dioxide thin films were coated by ALD on the porous anodic aluminum oxide. ALD films were influenced by the deposited interface morphology between Al₂O₃ and TiO₂ and narrow channel of ~ 10 nm was obtained by controlling ALD cycle.

1. Introduction

TiO₂ is a material that has been widely studied due to its application in electrochemical solar cells [1], chemical sensors [2], optical coatings [3], biocompatible coatings for biomaterials [4], and corrosion protection coatings [5]. Because of the great interest, TiO₂ thin films have been prepared by all possible physical and chemical thin film deposition methods. However, in recent years, the Atomic Layer Deposition (ALD) has been attracted more. The unique, self-limiting, growth mechanism of ALD process gives better thickness control, coating uniformity and better film quality than other deposition techniques. Particularly, the application of biomaterials for drug delivery system (DDS) and solar cells has been required for large surface area. Also, Anodic Aluminum Oxide (AAO) has attracted much interest in various fields due to their regular structure with narrow size distributions of pore diameters and inter-pore spacing, porous alumina membranes are being extensively used for the fabrication of nanometer scale device [6-8]. In this study, AAO was used in order to enlarge a surface area of TiO₂ film and the pore diameter, one of the merits in the AAO formation process, could be easily controlled by varying the AAO process parameters such as the anodizing voltage, electrolyte, temperature and time [9]. However, channels below ~10 nm were difficult to cast in AAO process. And hence, ALD will be a means in order to solve this problem. In these studies, the inner channel in AAO was affected by the variation of aspect ratio and nano-tubular structure for the composition of nano-wire below ~ 10 nm can be fabricated by the ALD process.

2. Experimental Procedure

Anodization was carried out using a two-step method [10]. Before anodization an aluminum foil (99.999 %) was electropolished for a period of 30 seconds below 25 °C in the mixture of perchloric acid – ethanol (ratio 1 : 4) and the current was kept at a constant value of 1.5 A. The process of first anodization was carried out at a constant voltage in 0.3 M oxalic acid and the temperature of the
electrolyte was maintained at 5°C. During the anodization process the solution was stirred using a magnetic stirrer in order to accelerate the dissipation of the heat evolved from the sample. The mixing is important for preventing the increase in the localized temperature and to maintain the stable growth of the anodic oxide film [11]. After 10 hours, the anodized oxide films were washed in the de-ionized water for 2 minutes. The aluminum oxide formed during the first anodization was removed by the etching process using phosphoric acid – chromic acid (ratio 1.8 : 6) for 5 hours at 60 °C. The second anodization was carried out in 0.3 M oxalic acid at 5 °C at a constant voltage of 40 V for 38 min and this was cascaded by the treatment of pore widening which was carried out in 0.1 M phosphoric acid for 40 min. the reactant was operated under a pressure of about 1.5 Torr using argon gas as carrier and purging gas. Ti(OC(CH₃)₂)₄ (Titanium (IV) Isopropoxide, UP chemical) and water were used as the precursors. TiO₂ was deposited using alternating exposures of Ti(OC(CH₃)₂)₄ and H₂O. One AB cycle consisted of a Ti(OC(CH₃)₂)₄ exposure, a Ar purge, a H₂O exposure, and a second Ar purge under 150 °C. The reactant gas source could easily be switched between the reactant exposure and the Ar purge using automated on-off valve. The Ar purge is required to remove the previous reactant and to avoid chemical vapor deposition.

3. Results and Discussion

a) Formation of Anodic Aluminum Oxide (AAO) for a substrate material. The observed AAO structure consists of an array of uniform nano-pores and with high aspect ratio. The formation of nano-porous structure is attributed to an equilibrium process that occurs at the alumina/electrolyte interface due to the field-enhanced oxide dissolution and oxide generation at the metal/alumina interface [12]. Figure 1 shows SEM image of the anodic aluminum oxide (AAO) and insert image was top view of AAO. Anodic oxide films were obtained by the two-step anodization [10]. The diameter and length of AAO was ~ 55 nm and 2µm, respectively. Constant anodizing voltage in Oxalic acid was carried out at 40 V. The quality of the ordered structure depends on the anodization voltage, which corresponds to the oxidation parameters given by Masuda and Fukuda [10].

![Fig 1 SEM image is porous anodic alumina. Porous structure was carried out in 5°C Oxalic acid at 40V constantly. Insert image is top view.](image)

b) Atomic Layer Deposition (ALD) of TiO₂ on AAO. TiO₂ films were deposited on porous anodic alumina with Atomic Layer Deposition. The result of experiments shows that the uniform nano-size channels and TiO₂ were successfully deposited on AAO template. Figure 2 shows the cross-sectional view of morphology of the deposited TiO₂ films according to the ALD cycles and insert image is the top-view of the sample. The ALD process was repeated 100 cycles (a), 200 cycles (b) and 400 cycles (c), respectively.
The deposited thickness per 1 cycle was approximately 0.5 Å in 150 °C and the variation of TiO2 films was observed by increase of the number of the ALD cycle. The pore-size control which has range of ~ 10 nm according to the ALD cycle was possible and TiO2 films with the uniform pore on the basis of the ordered AAO have larger surface area than that of flat surface. The channel size of TiO2 films was diminished from ~ 50 to ~ 20 nm in Figure 2. However, upper part and bottom part of TiO2 channels were presented the difference of diameter, because of the short flow-length of the reactant gas which was caused by high aspect ratio

\[ Q = n \nu A \]  

(1)

Where \( Q \) is gas flow rate, \( n \) is gas density, \( \nu \) is veracity of gas stream, and \( A \) is area of the channel. Gas flow rate and area of the channel were proportional \((Q \propto A)\). Gas flow rate was diminished by reason of the decreased area of inner channel according to the increase of the ALD cycle as a result. Reactant gas was fudged before it was arrived at the bottom because the short flow-length results from the reduced gas flow rate. After 400 cycles of the ALD process, upper part pore will be blocked due to the difference of the deposition rate in inner channel. So the deposition of TiO2 in inner channel will be stopped.

Figure 3 a schematic illustration shows the variation of TiO2 layer morphology according to the number of the ALD process.

Figure 3 shows the schematic illustration of the change of TiO2 layer in order to explain transformation between upper and bottom channel. Figure 4 shows the energy dispersion spectroscopy data. Figure 4 (a) is represents the EDS data of the AAO template which has no TiO2 films. Ti peak was not detected in figure 4 (a). The intensity of a Ti peak after the repeated ALD process was increased approximately in a region of 4.5 keV.
4. Conclusions

TiO$_2$ layer on porous anodic alumina template was grown on AAO by ALD process under 150 °C. The morphology of surface and the existence of TiO$_2$ layer have been studied with SEM, EDS. Thickness of TiO$_2$ was controlled by the number of AB cycle with ALD process. The deposited thickness per one cycle was approximately 0.5 Å and the decreased channel size was from ~50 nm to ~20 nm. Ti and O material was detected by EDS and approximately in a region of 4.5 keV. Pore size and depth of porous structure of TiO$_2$ can adjust by fabricating AAO template of the desired form. The inner channel size can be controlled by the AB cycle number.

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Advances in Nanomaterials and Processing
10.4028/www.scientific.net/SSP.124-126

Fabrication of Porous Al₂O₃ and TiO₂ Thin Film Hybrid Composite Using Atomic Layer Deposition and Properties Study
10.4028/www.scientific.net/SSP.124-126.1273

DOI References
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