

A New Fabrication Method of Aluminum Nanotube Using Anodic Porous Alumina Film as a Template

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Aluminum nanotube has been fabricated by a physical vapor deposition/atmospheric pressure injection using an anodic porous alumina film as a template. The pore external-, and inside diameters and the length of the aluminum nanotubes fabricated by this method are 60 nm, 35 nm and 2 μ m, respectively. The structure of the fabricated aluminum nanotubes was examined by a kind of chemical treatment as extraction of copper on the cross-sectional area of these aluminum tubes in a mixed solution of CuCl_2 and HCl by difference of ionization tendency between aluminum and copper. The composition of the aluminum nanotube was identified by the two dimensional Hybrid Plasma Equipment Model (HPEM) employing the inductively coupled plasma.

Key Words : Aluminum nanotube, Porous alumina film, Atmospheric pressure injection, HPEM

Introduction

In recent years, many studies have been focused on the fabrication of nanostructures such as nanotube, nanowire, and nanodot of various materials because of their potential for technological applications. For raising commercial application of these nanostructured materials, low cost and high-efficiency production methods are required. With the consequence, many methods for fabricating nanostructured materials of these types have been continually developed ranging from electron beam lithographic techniques to chemical methods.^{1,2} Among these methods several lithographic techniques using an optical^{3,4} or electron beam,⁵ atomic force microscope (AFM),⁶ and scanning tunneling microscope (STM)⁷ have been tried on fabrication of nano-devices in small batches. However, these methods are ineffective to be applied to a large scale of devices and a large output because of high cost and low output.

For this reason, many efforts have been tried to look for alternative methods to apply to nano-manufacturing. The template-synthesis⁸ is suggested among the alternative methods using the nanoporous materials as a template. There are appropriate candidate materials such as zeolites and molecular sieves,¹ polymer nuclear track membrane,⁹ porous anodic alumina membrane^{10,11} and others^{12,13} for template of this type.

One of the most promising among these materials is an anodic porous alumina membrane, which has recently been attracted as a key material providing a possibility of fabrication of nanometer-scale structures.¹⁴⁻¹⁷ Up to the present, the several techniques have been applying to fabricate the metal nanotube as the techniques reported for fabricating a nanostructured material within the pores of a porous alumina film using such as electrochemical deposition,^{18,19} electroless deposition,²⁰ chemical vapor deposition,²¹ high pressure injection,²² and others.²³⁻²⁷

Recently, we are interested in the fabrication of metal

nanotubes of nanostructured materials, because such nanotubes display a good conductivity, a low electron work function and a superior optical property for the metal nanotube membranes with a sub-wavelength scale aperture. Furthermore, the metal nanotubes can be employed as field emission electrodes,^{28,29} quantum devices,³⁰ and memory devices.³¹ Also, these metal nanotube membranes show a possibility to be used as anode materials in lithium-ion batteries.³²

So far, the fabricating metal nanotubes tend toward to apply to the electrochemical and the electroless deposition method recently. However, these two methods imply some difficulties in the chemical synthesizing process that they entail inevitably a variety of suitable chemical processes for synthesizing metal nanotubes. For example, in the case of electrochemical deposition method, it must be derived chemically the pore wall so that a desired metal preferentially to deposit on the pore wall typically. Also, electroless deposition method involves a difficult process of treating a chemical reducing agent to plate a metal from solution onto a pore wall surface. Moreover, these two methods are accompanied by another difficulty so that they must be controlled the deposition time, because a hollow metal tube can be obtained within each pore after short deposition time, while long deposition times result in solid metal nanowire.

We report here a new alternative method termed as "two step evaporation method" to fabricate metal nanotubes using a porous alumina film as a template. This method entails an evaporating process which forces to inject aluminum vapor into the pores of a porous alumina template using the atmospheric pressure.

Experimental Section

Preparation of Anodic Porous Alumina Film. High purity aluminum sheets (99.999%, 25 \times 25 \times 0.5 mm) were used as the starting material for preparation of anodic porous

alumina film. First, the aluminum sheet was degreased in acetone and annealed under the atmosphere at 500 °C for 20 min in order to obtain homogeneous conditions for pore growth over large area. Subsequently, the sheet was mechanically polished to remove the oxide layer formed on the surface and to smooth the surface morphology finally with diamond suspension of 0.25 μm . The mean roughness of the polished surface was about 3 nm over a 3 μm square scan area as measured by atomic force microscopy (Auto Probe CP research, PSTA Co).

The anodic porous alumina film employed here was prepared by the two-step anodization method²² to make a thin porous alumina film which is applicable as the template for physical vapor deposition. The first-step anodization of aluminum was conducted in a 0.3 M oxalic acid solution at 4 °C for 2 h at the constant voltage of 40 V, and the second-step anodization for 30 min under the identical conditions to those for the first-step anodization. After two-step anodization, the surface oxide layer, on which pore entrances were very narrow or nearly closed, was etched by immersing the sample in a 5 wt% phosphoric acid at 30 °C for 10 min to widen the surface pore entrances. Then the aluminum substrate was removed in a saturated HgCl_2 solution. The pore diameter and thickness of the resulting film were about 60 nm and 2 μm , respectively.

Synthesis of Aluminum Nanotubes. We developed a new method termed "two step evaporating method" for fabricating metal nanotube using an anodic porous alumina film as a template. The fabricating process of aluminum nanotube arrays using this method is shown schematically in Figure 1. This method consists of two evaporation steps. *i.e.* the first step is an aluminum evaporating process for depositing aluminum on the surface of the porous alumina template in vacuum, and the second step is a heating process of the aluminum sample which is deposited on the surface into the pores under the atmospheric pressure for injecting as

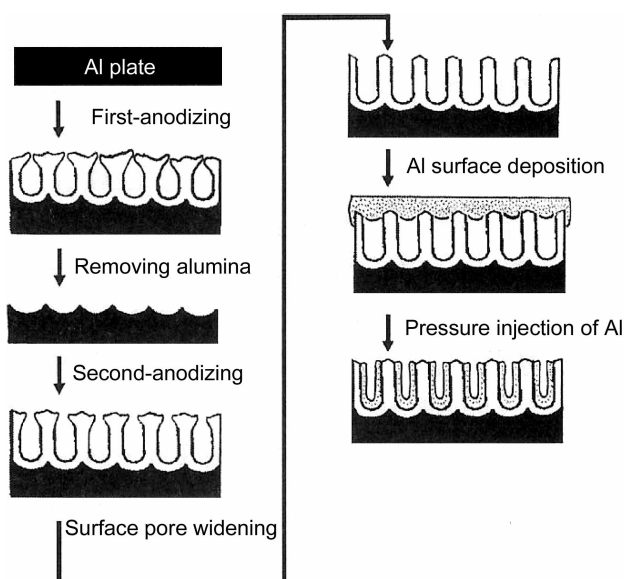


Figure 1. Schematic process for fabrication of aluminum nanotube.

the vapor state.

Aluminum was first deposited onto the surface of the porous alumina template by thermal evaporation in vacuum of 5×10^{-6} torr until the pore entrances were completely blocked by the deposited aluminum layer. Subsequently, this aluminum-deposited sample was transferred to an electric furnace keeping a temperature of *ca.* 700 °C under the atmospheric pressure, and heated for about 10 s. Here the purpose of sample heating is to evaporate the aluminum deposited on the template surface, and here, the atmospheric pressure plays as the role which forces to inject aluminum vapors into pores during the second-step evaporation. Soon after this evaporation, the resultant sample was taken out of the furnace for air cooling.

Temperature of the boat was measured by portable radiation thermometer (IR-AH, Chino Co.). FE-SEM images of anodic porous alumina film and aluminum nanotube structure was observed with a Hitachi S-4200 Field-Emission Scanning Electron Microscope.

Results and Discussion

Figure 2 shows FE-SEM image of a typical porous alumina film formed by two-step anodization used as a template for fabrication of aluminum nanotube. This figure shows that the surface of the resulting film is composed of pores with narrow or nearly closed entrance. A difficulty was accompanied by such a surface pore structure in making the injection of the aluminum vapors into the pore channel during thermal evaporation. Figure 3 shows a SEM image of top surface after surface pore widening by chemical etching treatment. As shown in this figure, the measured pore diameter is enlarged to about 60 nm from the prepared pore size soon after pore widening. After this surface pore widening treatment, a sufficient amount of aluminum was evaporated on the surface of the resulting sample until pores were completely covered by the deposited aluminum layer. Figure 4 shows the SEM images of a cross sectional view(a), a top-surface view(b) and the inside view(c) of nanotube of an anodic porous alumina film after the first-step evaporation,

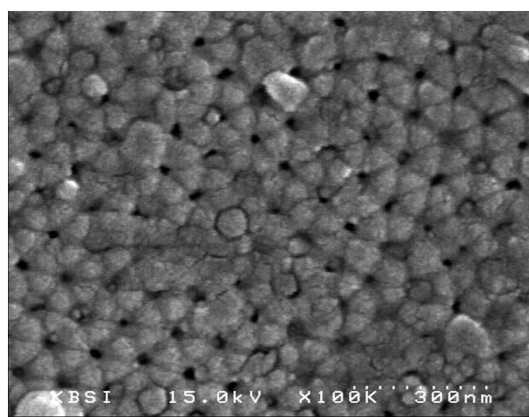


Figure 2. FE-SEM image of the top surface view of the typical porous alumina film after two step of anodization in a 0.3 M oxalic acid solution at 4 °C at 40 V.

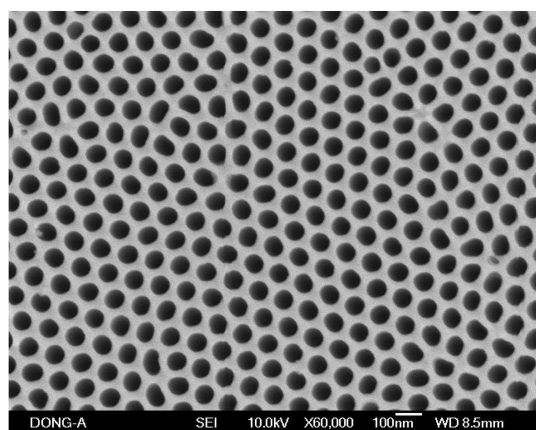


Figure 3. FE-SEM image of the top surface view of the porous alumina film after pore widening treatment by 5 wt% phosphoric acid.

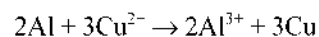
respectively.

In Figure 4, the thickness of deposited aluminum layer was measured at about 200 nm. As shown in these figures, the surface pore entrances are completely blocked by the aluminum-deposited layer, and the pores still remain hollow without leaving any trace of aluminum deposition on the inside wall of pore. It means that a sufficient amount of aluminum vapors to form tube was not injected into the pores in the first-step evaporation, because the pore entrances were rapidly blocked by the aluminum-layer deposited on the template surface in the early stage of evaporation. Accordingly, it is necessary to use other method in order to give a high-pressure aluminum vapor into the pores.

The aluminum which had been deposited on the template surface top was heated in an electric furnace at the temperature of *ca.* 700 °C under the atmospheric pressure. Even though the sample has been exposed to the atmosphere, the inside of pores would be still maintained a vacuum state of the order of 10^{-5} torr due to the sealing effect by the aluminum layer blocking pore entrances until pore entrances opened by the second step evaporation. Soon after the aluminum vapor was injected at the second step, a SEM image of cross sectional view was observed as shown in Figure 5(a). The pore inside diameter and interpore distance are about 35 nm and 100 nm, respectively in this figure.

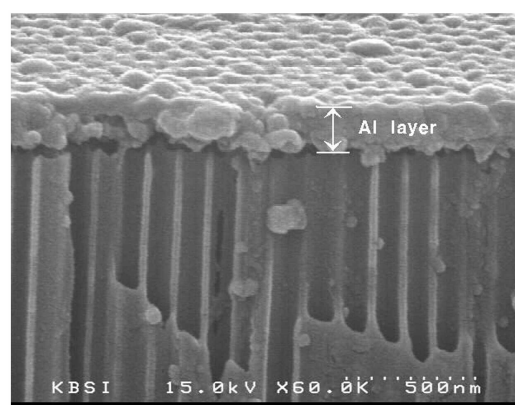
It was also examined to confirm the structure of aluminum nanotube from the observation of any change of pore structure produced by chemically treating the resultant sample after the second step evaporation.

Firstly, the resultant sample after second step evaporation was broken into pieces, and then one of these pieces was dipped in a mixture of 0.1 M copper chloride (II) and 20 % (v/v) hydrogen chloride solution. If aluminum tubes were fabricated in the pores of this template, it would be expected that copper is extracted only on the cross-sectional area of these aluminum tubes by the substitution of copper for aluminum due to the higher ionization tendency of aluminum than that of copper as follows:

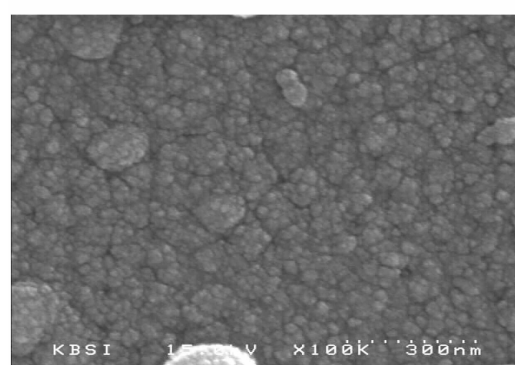


A cross-sectional view of the resultant sample after the second-step evaporation followed by chemical treatment in a solution of CuCl_2 and HCl is shown in Figure 5(b).

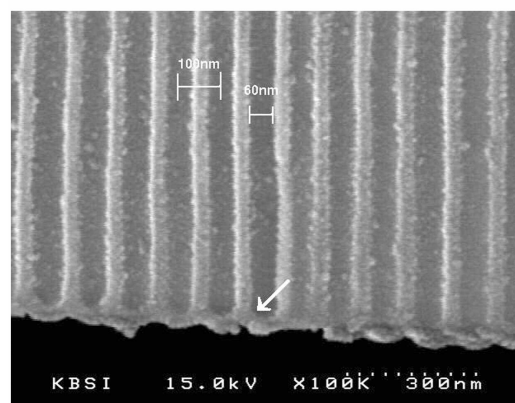
Comparing both two figures in Figures 5(a) and (b), we can see that the two SEM images are quite different from each other. It is shown that the both sides around a black column corresponding to the hollow cavity and the bottom



(a)

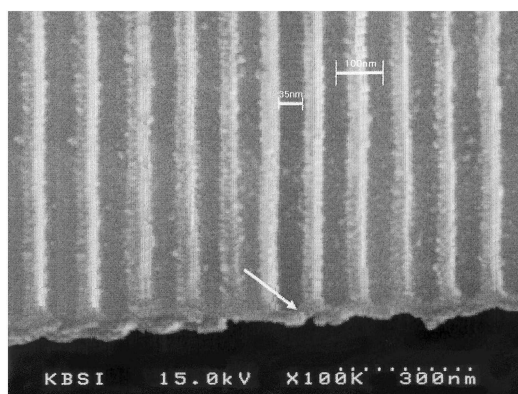


(b)

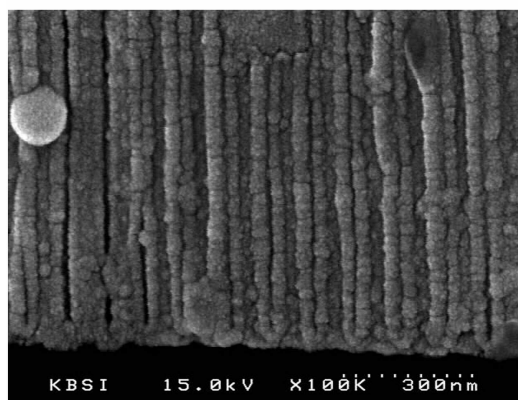


(c)

Figure 4. FE-SEM images of the aluminum-deposited porous alumina film after the first step evaporation: (a) cross-sectional view (thickness of the aluminum layer: *ca.* 200 nm), (b) top-surface view, and (c) the inside view of alumina nanotube in detail.



(a)



(b)

Figure 5. (a) FE-SEM image of the cross-sectional view of fabricated aluminum nanotube before a chemical treatment. (b) After injection of aluminum and chemical treatment for extraction of copper.

side are uniformly expanded with swollen form as shown in Figure 5(b).

The swollen "U" shape which points at the bottom of the pore with an arrow corresponds to the cross-sectional wall of an aluminum nanotube synthesized in a pore. It is clear that the both swollen stripes around a black column are accord with the cross-sectional walls of an aluminum nanotube in Figure 5(a). If the aluminum nanowires were synthesized instead of aluminum nanotubes the whole regions of the pore would be filled by a solid state of aluminum reasonably. It is nothing like there is a possibility to be observed as aluminum nanowires analogized with the results as shown in Figure 5. There is other evidence, that is, the aluminum tubes are proved clearly from the fact that the width of the swollen stripe is observed only about 35 nm as shown in Figure 5(b).

If they were synthesized as the aluminum wires, the width would be about 60 nm or more. However this possibility is not shown in the SEM images in Figure 5. Judging from these results of SEM observations, it is concluded that aluminum tubes were definitely synthesized in the pores, and this swollen form was originated from the volume expansion to be caused by the substitution of copper for aluminum on the cross sectional area of the aluminum tube

synthesized in the pore.

Other evidence shows clearly for the fabrication of aluminum nanotube as the distances between two hollow cavities and between two swollen adjacent stripes each other as shown in the SEM image in Figure 5(b) are almost same as the inter-pore distance and the pore diameter in the SEM image as shown in Figure 5(a), respectively. Likewise, the volume expansion is due to the result of substitution of copper for aluminum observed in the separated experimental result in this connection with this study. The enough evidence shows a fact that the wall thickness of aluminum tube is much thinner as the size of a few nm than that of the swollen stripe of 35 nm. In addition, the extracted copper could be observed even with an eye so that the copper was extracted on the cross-section of porous alumina template, while the surface area was changed to be dyed dark red.

To get the more conclusive and confirmative evidence for the aluminum nanotube fabricated the sample was tested by the two dimensional Hybrid Plasma Equipment Model (HPEM)^{33,34} employing the inductively coupled plasma. At first, the sample fabricated was cut sliced with knife thinly, placed on the tip of the inductively coupled plasma chamber and applied the magnetron power from 0.2 kW to 2.0 kW. As shown in Figure 6, each ionization fraction of the sample which is fabricated in this study decreases slowly from 0.78 to 0.65 for alumina with the magnetron power increases while, decreases steeply from 0.69 to 0.08 for aluminum respectively. And the total flux of aluminum increases from $0.78 \times 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$ to $1.85 \times 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$ and increases from $0.45 \times 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$ to $1.58 \times 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$ for alumina respectively with the magnetron power increases. The ratios of mass ion of analyzed amount for aluminum and alumina show as 5.64 and 1.70 and the ratio accords with the composition of the cross-sectional surface of the fabricated aluminum nanotube. This results show the ratio of aluminum and alumina is agree with the surface composition of the amount of aluminum and alumina clearly.

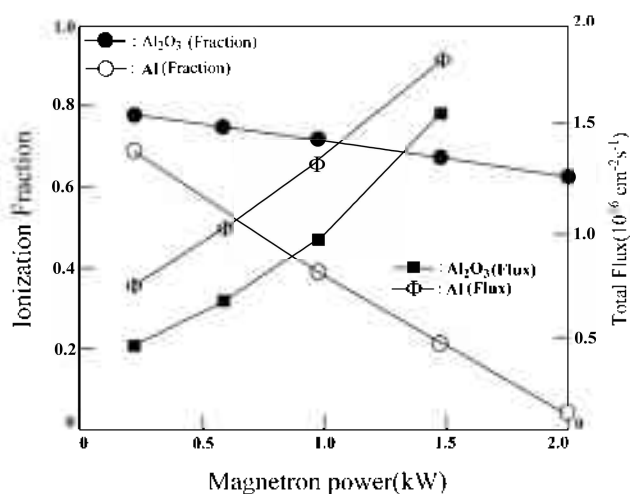


Figure 6. Ratios of ionization fraction and total flux for aluminum and alumina in the sample as a function of the applied magnetron power at 30 mTorr.

Pressure injection method is often employed when fabricating highly crystalline nanotubes from a low melting point material using a porous material as a template.³⁵ The essentials of this method are that a desired material in liquid form is forced to inject into the evacuated pores of the template by pressure.^{22,30-36} According to this method, the modestly applied pressure of 4×10^3 atm is required to overcome the surface tension effects which prevent the molten metal from entering the narrow pores of nanoscale diameter.^{22,37-39} Even though the high pressure is needed usually to fabricate the aluminum nanotube, however, in this study, the aluminum nanotubes could be fabricated under the atmospheric pressure which is relatively very low pressure as 1 atm compared to the pressure required for the fabrication of metallic nanotubes. Also, it is concluded that, our method for the fabrication of aluminum nanotube under such a low pressure is a quite different from the well-known methods based on the injection of molten metal which have been reported, and is contributed possibly to fabricate using metal vapor on the inside wall of pore directly.

Conclusion

We have developed a new way which can fabricate aluminum nanotube arrays by a physical vapor deposition/atmospheric pressure injection using an anodic porous alumina film as a template. It is firmly believed that this method can be applicable to the fabrication of nanotube arrays of various metals which can be evaporated in vacuum. As compared with the conventional chemical methods, this method shows an advantage which is simple and suitable for fabricating a special purpose of metal nanotubes.

In addition, the pore outdiameter and length of the aluminum nanotube fabricated by the present method are dependent on those of the anodic porous alumina film used as a template. Accordingly, this method displays also additional advantage that the control of the length and diameter of aluminum nanotube is possible by adjusting the pore diameter and length of the anodic porous alumina template.

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