나노허니컴 구조물의 제작 및 홀 사이즈 측정

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Fabrication of nanohoneycomb structures and measurement of pore sizes

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Abstract

A new method for measurement of the pore size in a nanohoneycomb structure using atomic force microscopy (AFM) was proposed. Porous type anodic aluminum oxide (AAO) was fabricated as a nanohoneycomb structure to measure the pore size. For measuring pore sizes from AFM images, a criterion was set in porous type AAO. The pore sizes from AFM images were compared with those from SEM images, and the results showed good agreement. The relationship between the pore size and widening time was found to be linear in the range of this study. It was understood as the synchronized effects of the impurity gradient in outer oxide of AAO, mechanical packing and mass transfer increase.

Key Words: Nanohoneycomb, Atomic Force Microscopy, Pore Size.

1. Introduction

In recent years, anodic aluminum oxide (AAO) film has attracted considerable attention due to its potential use in a new field, nanotechnology. There are barrier-type and porous-type films in the type of AAO film. The porous-type AAO film is considered a "nanohoneycomb" structure because its pore shape is similar to a honeycomb structure, but its pore size is typically a nanometer scale. Its extremely high aspect ratio and self-ordered hexagonal pore structure are the most attractivefeatures. Moreover, simple control of pore dimensions such as diameter, length and density by varying anodizing condition would be advantageous [1].

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Nanohoneycomb structures have unique physical, chemical, optical and magnetic properties [2]. It is necessary to determine the exact pore geometry to effectively characterize the structures because those properties are affected by the pore size. SEM is used most generally to measure the pore size [3]. There are some methods using TEM [4], replica [5], or the others [6]. However, these methods are destructive and require specific material properties. The materials are generally conductive for using SEM, and the samples are destroyed for using TEM.

Atomic force microscopy (AFM) has been given a great deal of attention by researchers who study surface topography, frictional properties andmagnetic properties at the nanometer scale because of its various applicable modes and its unique advantages. AFM measurements are nondestructive and all materials can be used as specimens. However, there is the distortion of an image referred to convolution effects in AFM measurements. It comes from the geometric shape of a tip. If the specimen has the vertical step, the image from AFM becomes the V shape. Therefore, the geometrical dimensions of specimens can't be obtained directly from AFM images without additional information of the specimen.

Porous-type AAO film has been studied by AFM [7], but the AFM images have never used to measure the pore size because of the convolution effects. When the surface properties of nanohoneycomb structures having pores such as porous-type AAO films are studied, it is necessary that the pore size of the specimen is measured without destroyed or coated. Therefore, in this study, a new method for measuring pore sizes with AFM is investigated. The results are compared with those of SEM. After the pore sizes are determined, pore widening rate is also considered.

2. Determination of a Criterion to measure Pore Sizes with AFM

Although the top surface of porous-type AAO films has been flat in the schematic diagram of many researches, the top surface is not actually flat. The cross section of the porous-type AAO film can be shown schematically as the solid line in Fig. 1. A material in isotropic wet etchants is generally etched in all directions at nearly the same rate, but it was found in many tests that the etching rate for the surface of the porous-type AAO film was much slower than the rate of the pore wall as dashed lines in Fig. 1. Unfortunately, the etching rate for the surface of the porous-type AAO film could not be obtained because the surface of the porous-type AAO was very irregular.

Fig. 2(b) shows the cross section of a porous-type AAO film measured by AFM. The pore wall is actually straight as shown in Fig. 1, but it is curved in an AFM image. Therefore, the pore size can not be determined from the AFM image without a criterion. In this study, the vertical depth between the top of a surface and the pore

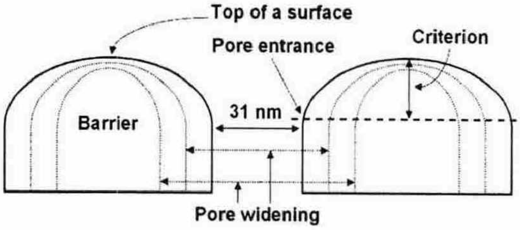

Fig. 1 Schematic diagram for pore widening of a porous-type AAO film.

entrance for the specimen without widening is chosen as the criterion because the etching rate of the surface is very slow, and the variation of the pore size is very large. As the pore is widening, the variation is larger. Therefore, although the criterion makes the error of the pore sizes, the error may not affect the average of the pore size because of the large variation

3. Experimental Procedure

A pure Al sheet (99.999 %) with a thickness of 1mm was electropolished in a mixture of perchloric acid and ethanol ($HClO4:C2H5OH = 1 : 4$ in volumetric ratio) to remove surface irregularities. The specimen was used as an anode while a flat Pt was used as a cathode. A constant voltage of 20 V was applied between the cathode and the anode for 60 ~ 90 sec and the solution temperature was maintained at 7 °C during electropolishing. After electropolishing, the first step anodization was carried out in a 0.3 M oxalic acid solution for more than 2 hours (typically 10 ~ 12 hours). The AAO layer was then removed by immersing the specimen in a mixture of 1.8 wt% chromic acid and 6 wt% phosphoric acid at 65 °C for 1 ~ 4 hours. Finally, porous-type AAO films were obtained by the subsequent second anodization under the same condition as the first one. After porous-type AAO films are fabricated, the pores are widened by etching in a 0.1 M phosphoric acid solution at 30 °C. The widening times are 0, 20, 30, 40, 45 and 50 minutes. Fieldemission scanning electron microscope (FE-SEM, JEOL JSM-6330F) and atomic force microscope (AFM, Seiko SPA 400) are used to measure the pore size. The specimens for FE-SEM are coated with Pt. In AFM, the surface was scanned under non-contact mode with a Si cantilever (SEIHR) which has a tip radius less than 10 nm and typical bending stiffness of 10 N/m fabricated by Nanosensors company.

4. Results and Discussions

4.1 Measurement of pore size with FE-SEM and AFM

Three specimens which have etching time of 0, 30, and 50 minutes were prepared for the measurement of a pore size. Fig. 2 shows the top view and the cross section of the porous-type AAO film by AFM. The original pore size of the AAO film before widening was measured about 31 nm by FE-SEM in agreement with Nielsch's [4] result using TEM. The criterion to obtainthe pore sizes by AFM is then measured by the next procedure.

a) Find the positions where the pore size becomes about 31 nm, the distance (①) between the vertical dash lines in Fig. 2(b).

b) Measure the vertical depths (② and ②' in Fig. 2(b)) between the top of a surface and the pore entrance. The positions of ① should be controlled to make the vertical depth in the left (②) and the right (②') equal. In this study, the average of the vertical depths obtained from about one hundred different measurements was 10.5 nm as the criterion.

After the criterion is determined, the pore sizes are measured by the reverse order of the procedure to obtain the criterion.

a) Find the positions where the distance between the top of the surface and the pore entrance is 10.5 nm in the other AFM images. The pore entrances are the positions crossing of the vertical dash lines and the horizontal dash line in Fig. 2(b).

b) Measure the distance between the pore entrances. The distance is the pore size.

Fig. 3 shows the pore sizes and standard deviations for each AAO film measured from SEM images and AFM images. The pore size for the specimen without widening was again measured by using the criterion. The results showed good agreements. The pore size of the specimen etched for 50 min was a little smaller in AFM measurement than in FE-SEM measurement. It was why the surface of porous-type AAO film was etched actually. However, the pore sizes measured in AFM could be acceptable because the discrepancy in the measurements is very small compared with the variation of the pore size in each measurement.

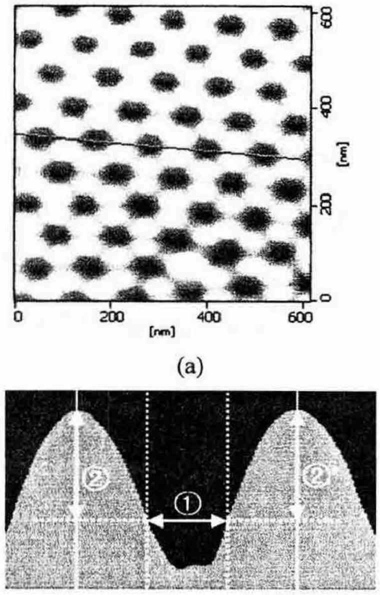

Fig. 2 (a) A top view and (b) a cross section of porous-type AAO film by AFM.

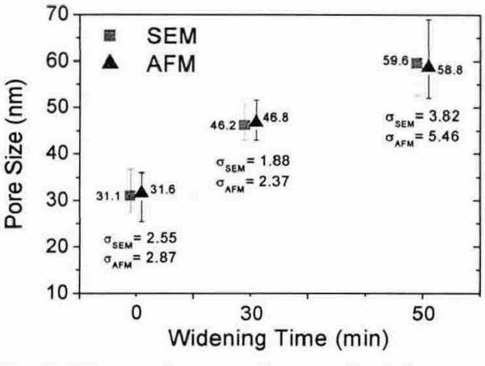

Fig 3 Measured pore sizes and their standard deviations.

4.2 Measurement of pore widening rate

The specimens which have etching time of 0, 20, 30, 40, 45 and 50 minutes are used to calculate the pore widening rate. The pore sizes were measured from AFM images. Fig. 4 shows the measured pore size vs. the widening time. It was found that the pore widening rate was linear. It may be explained by an impurity gradient in the outer oxide of AAO, mechanical packing and an increase in mass transfer. A porous-type AAO film consists of duplex structure of inner and outer oxide layers [8-9]. It is known that the inner oxide layer is composed of pure alumina, whereas the outer oxide layer has impurities such as incorporatedanions. Because of the gradient of impurities in the outer oxide, the longer the etching time is, the slower the etching rate is. Moreover, because the inner part of the layer is more tightly packed mechanically, the etching rate is also slower. On the other hand, as the pore widens, the etching solution contacts a larger surface of pore wall and the mass transfer for etching is then accelerated. Thus, the etching rate increases. After all, it is believed that the synchronized effects of both the increase and the decrease in etching rate create the widening rate linear relationship.

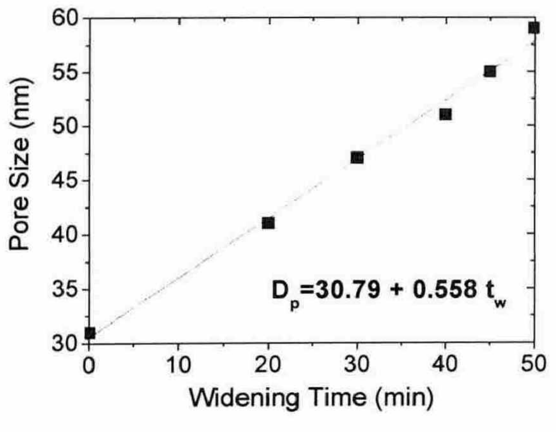

Fig. 4. Pore widening rate. The relationship between pore size and widening time was linear.

5. Resutls and Discussions

In this study, the criterion to measure the pore size by AFM was determined. The pore sizes obtained by AFM images showed good agreements with those by SEM images. Pore widening was found to depend linearly on the etching time. It was understood due to synchronized effects of impurity gradient in outer oxide of AAO, mechanical packing and mass transfer increase.

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