Available online at www.sciencedirect.com
SCIENCE DIRECT®
Current Applied Physics 6S1 (2006) e125–e129
Current Applied Physics
An official journal of the KPS
www.elsevier.com/locate/cap
www.kps.or.kr

Measurement of the pore sizes for anodic aluminum oxide (AAO)

D.H. Choi [a], P.S. Lee [b], W. Hwang [a,*], K.H. Lee [b], H.C. Park [a]

[a] Department of Mechanical Engineering, Pohang University of Science and Technology, San 31, Hyoja Dong, Nam-gu, Pohang, Kyungbuk, 790-784, Republic of Korea
[b] Department of Chemical Engineering, Pohang University of Science and Technology, San 31, Hyoja Dong, Nam-gu, Pohang, Kyungbuk, 790-784, Republic of Korea

Received 5 August 2005
Available online 9 March 2006

Abstract

A new method for the measurement of pore size of the porous-type anodic aluminum oxide (AAO) using atomic force microscopy (AFM) is proposed. The measurement of the pore size by AFM makes no damage to the specimen. AAO film can be referred as a nanohoneycomb structure because the pore shape of AAO is like the honeycomb structure and its pore size is in the nanometer scale. To measure the pore sizes from AFM images, it is assumed that the top surface of AAO is not etched much in the pore widening process. It is because the etching rate of the top surface is very slow due to the mechanical packing stress in the middle of the pore wall of AAO. The pore sizes from AFM images showed good agreement with those from SEM images.

PACS: 06.30.Bp; 07.79.Lh

Keywords: Anodic aluminum oxide; Atomic force microscopy; Pore size; Pore widening; Mechanical packing stress

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 AAO film. The porous-type AAO film is generally called as AAO film. AAO film is considered a "*nanohoneycomb*" structure because the pore shape of AAO is similar to a honeycomb structure, and its pore size is typically in a nanometer scale. Its extremely high aspect ratio and self-ordered hexagonal pore structure are the most attractive features. Moreover, it is advantageous nature of AAO film that pore dimensions such as diameter, length and density can be controlled by varying the anodizing condition [1].

The initial pore size of AAO depends on the acid solution used in the anodization process as reported in many previous sources. The pore size of AAO is increased by the etching process. Because the various properties of the AAO film depend on the pore size [2–4], it is necessary to adjust the pore size of AAO and it is important to measure the pore size. SEM is used most widely to measure the pore size [5–7]. There are some methods using TEM [8], replica [9,10], and others [11,12]. However, these methods are destructive and material property dependent. The specimen has to be conductive to be measured with SEM, and has to be destroyed to measured with TEM.

Atomic force microscopy (AFM) has been given a great deal of attention by researchers, who study surface topography, frictional properties and magnetic properties in the nanometer scale because of its various applicable modes and its unique advantages. AFM measurements are nondestructive and wide range of 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. Even if a specimen has the vertical step (_⎍⎍_), the image from

---

[*] Corresponding author. Fax: +82 54 279 5899.
E-mail address: whwang@postech.ac.kr (W. Hwang).

doi:10.1016/j.cap.2006.01.024

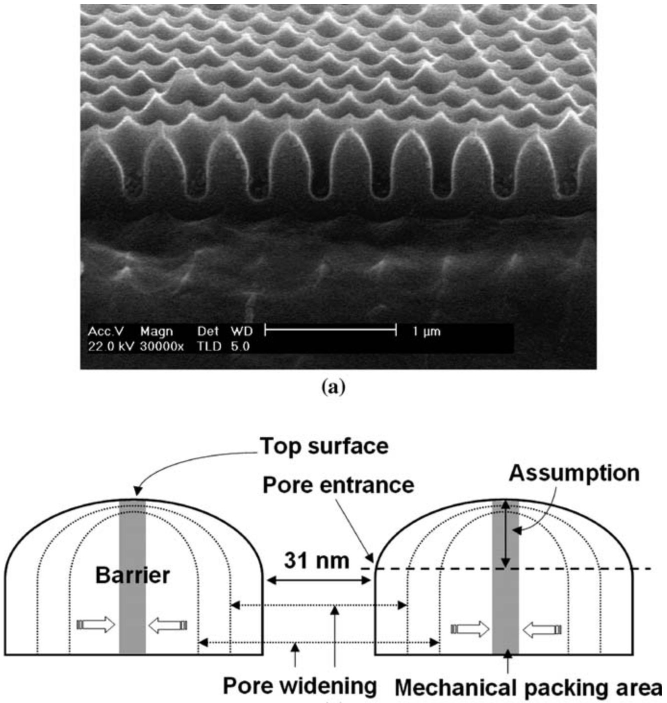
AFM becomes the V shape (). Therefore, all geometrical dimensions of specimens cannot be obtained from AFM images.

In this study, a new method for measuring the pore size of AAO with AFM is investigated. AAO film is fabricated by perchloric acid, and it is widened by phosphoric acid. Because the etching rate of the top surface of AAO is much slower compared with the etching rate of the side wall of AAO, it is assumed that the top surface of AAO is not etched much. To verify the proposed method, the results from the AFM images are compared with those of SEM.

2. Etching rates in AAO

Although the surface of AAO has been flat in the schematic diagram of many researches, the top surface is not actually flat. Fig. 1(a) shows the cross section of AAO film, which is fabricated by two step-anodizing at 195 V in a 0.1 M phosphoric acid at 0 °C. The surface of AAO can be considered a crown shape. 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 of the top surface of AAO was much slower than the rate of the pore side wall, as shown in dashed lines of Fig. 1(b). It is due to the mechanical packing stress is applied to the middle of the pore wall of AAO, as shown in Fig. 1(b) [12,13]. When the mechanical packing stress applies to the material, the etching rate becomes slow because the packed part is denser than the other parts. Unfortunately, the etching rate of the top surface of AAO could not be obtained because the surface of the porous-type AAO was very irregular.

Fig. 2 shows the top view and the cross section of AAO measured by AFM. The pore wall is actually straight, but it appears as a curved line in the AFM image. The pore size cannot then be determined from the AFM image. In this study, it is assumed that the vertical height (see Fig. 1(b)) between the top surface and the pore entrance did not change much during the etching process because the etching rate of the top surface is much slower compared with the etching rate of the pore of AAO in the pore widening process.



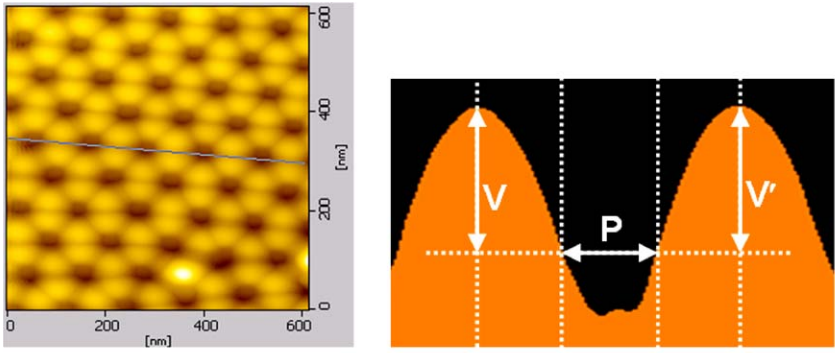
(a)
(b)

Fig. 1. (a) SEM image of AAO in side view and (b) schematic diagram of the pore widening of AAO. The top shape of AAO is like the crown.

3. Experiments

3.1. Fabrication of AAO film

A pure Al sheet (99.999%) with a thickness of 1 mm was electropolished in a mixture of perchloric acid and ethanol ($HClO_4$:C_2H_5OH = 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 s 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 h. 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



(a)
(b)

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