Synthesis and characterization of nanoporous alumina films with controlled physical and chemical attributes

N.A. Monfared*, S.V. Atre*, R. Kishton**, S. Varadarajan**

*Oregon State University, Corvallis, OR, USA
MIME School, 204 Roger's Hall, abolhasn@onid.orst.edu & Sundar.Atre@oregonstate.edu
** University of North Carolina, Wilmington, NC, USA

ABSTRACT

The performance of nanoporous surfaces are highly dependent on the pore's morphology, size and chemistry as well as their density and homogeneity. Therefore it is important to be able to control these factors.

There are several methods to make nanoporous structures. Among them, self-organizing structures, have potentially the highest versatility and are relatively easy for fabrication. Anodized alumina which provides noticeable characteristics such as uniformity, high pore density, and controllable pore dimensions could be a good choice for many different applications.

In this study, a protocol was developed to identify the key design rules governing the synthesis of alumina films with controlled nanoporous structure, by anodizing aluminum. The identification of key design rules and quantification of their effect on nanoporous anodized alumina, will lead to manufacturing tailored, pre-designed porous structures, by avoiding the trial-and-error procedures.

Keywords: Nanoporous, alumina, membrane, anodizing, design rules

1 INTRODUCTION

Unique electronic, magnetic, and optical properties of nanostructured materials have attracted much interest in recent years [1]. Nanoporous surfaces and nanostructured membranes provide large surface area which is useful in many applications, such as sensors [2-5], filters [6], catalysts [7-10], drug delivery systems [11, 12], tissue engineering [13-18], templates for manufacturing of nanotubes, nanowires [19, 20] or other nanoporous surfaces and nanosize membranes. [21, 22] In all applications of nanoporosity, the morphology and dimensions of pores, besides the surface chemistry of pores are main factors to improve device performance. [5, 18, 19, 23, 24] In order to enhance performance, the nanoporous surface should be designed and engineered properly by considering the application of device and the working media.

Another important requirement is the need for volume manufacturing of nanoporous surfaces with specific attributes. For this purpose, material and method selection is the initial step. The material should provide the required properties of device and the method needs to be practical, accurate, repeatable and able to provide the tunability in fabrication of device. Although there has been considerable evolution and growth in fabrication of nanostructure materials and devices, several difficulties remain due to complex manufacturing process and the lack of ability in controllable incorporation of nanosize components into devices [5].

In this study, the anodizing of aluminum thin film was chosen as the fabrication method in applications based on nanoporous alumina membranes. In this method, the morphology and dimensions of the porosity were changed by applying different conditions during the anodizing process. Some variables that were studied include anodizing duration, temperature, applied potential, stirring rate, electrolyte chemistry and its concentration. By monitoring the effect of each variable and the effect of them in combination with each other, the identification of design rules would be achievable. By identifying the governing rules controlling the properties of the alumina nanoporous membrane properties it will be possible to eliminate the trial-and-error cycle for new product requirements.

2 EXPERIMENTAL

2.1 Materials and Method

Two step anodizing of aluminum [24] was selected as nanoporous surface fabrication method. Alumina produced by anodic oxidation (anodizing) has a highly ordered, self organized, nanoporous structure which makes it very desirable method to fabricate a nanoporous surface [6, 25, 26].

Aluminum samples prepared for anodizing were 500 nm aluminum (0.5% Cu) deposited on silicon wafer by using the sputtering method. A 200-300nm titanium layer was used to provide good attachment of aluminum layer to the substrate. This sample was used as the working electrode (positive electrode, anode) during anodizing.

The cathode was 314 stainless steel. A saturated calomel electrode (SCE) was used as the reference electrode. The galvanostatic anodizing was done in an electrolyte solution of oxalic acid. Concentration of oxalic

acid was considered as one of the variable factors and in three different series of experiments 0.3 wt%, 1 wt% and 3 wt% oxalic acid were used. In each concentration series three different anodizing potentials of 40, 50, and 60V DC were applied. All tests were done at room temperature, 10 and 0˚C. The effect of anodizing durations was also investigated and for each condition samples were tested in at least 3 different times. A typical anodizing cell and the variable parameters are shown in Figure 1.

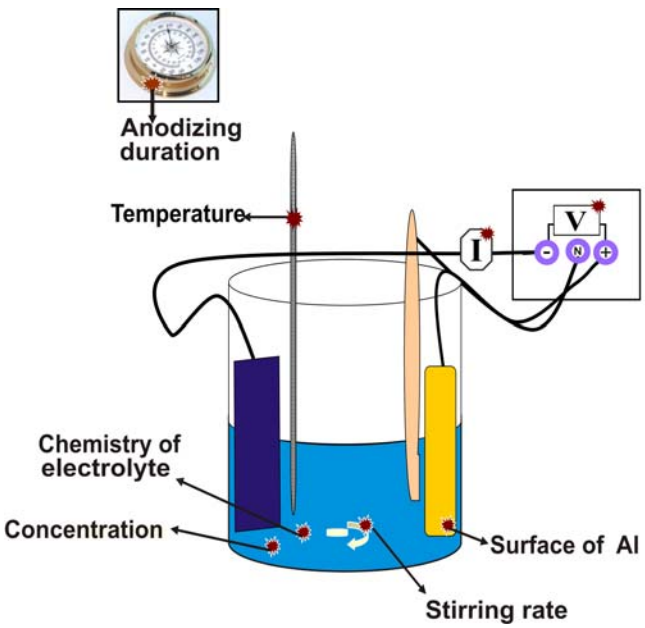


Figure 1: Anodizing cell and anodizing variable parameters.

After first anodizing, the anodized surface layer of all samples was removed. For this purpose a solution of phosphoric acid 6wt% and chromic acid 1.8 wt% was heated to 50˚C and poured on each anodized surface. After 5 to 7 minutes, the samples were washed with deionized water properly and dried with compressed air.

After removing the first anodizing layer, all samples are anodizing for second time in same electrolyte concentration that first anodizing were done for each sample. In all experiments, the second anodizing step was done in room temperature, for 60 minutes.

2.2 Design of Experiments (Taguchi Method)

The typical approach to experimental studies with more than one variable is changing one factor at a time while other factors are kept fixed. Increasing the number of variables will increase the experiment runs in a factorial manner.

By using fractional factorial methods, the number of runs required for the study will significantly decrease. Reducing the number of test runs by using fractional factorial design, helps to decrease both time required for the study and its related expenses.

The Taguchi method is an effective technique based on the fractional factorial design methods. This method is used in the present study as the design of experiments (DOE) approach. This method is a robust statistical technique with proven reliability [27, 28]. The Taguchi method is simple and efficient, and generates a systematic approach for optimization. The Taguchi method indicates that the appropriate orthogonal array depends on the given control factors and their acceptance states, their interactions, their degree of influence, desired resolution, and available resources. Based on this orthogonal array, data are collected for analyzing the experimental results.

For the current test set up, changing the 4 variables of time, temperature, voltage and concentration of electrolyte, while each of them accept 3 states in average, will need at least 3^4=81 experiments for first anodizing step. In such case, the Taguchi method suggests a L_9 orthogonal array which decreases the experimental runs to 9. Table 1 shows variable factors and their selected states, and Table 2 is the test design based on the Taguchi method.

2.3 Characterization

During all anodizing steps, the current changes were measured and recorded. The temperature changes during the experiments were also controlled.

For evaluating the nanoscale structure of anodized samples and investigating the effect of different parameters on these structures scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used after each step.

SEM characterization of the membranes was performed using a Hitachi S-4700 Cold Cathode Field Emission Scanning Electron Microscope. The SEM was conducted using a 5 kV accelerating voltage, and 10–11 mm working distance.

Variables and their states	Voltage (V)	Temperature (˚C)	Time (minutes)	Oxalic acid concentration (wt%)
1	40	25	10	0.3
2	50	15	60	1
3	60	0	120	3

Table 1: Considered variables and their states

NSTI-Nanotech 2009, www.nsti.org, ISBN 978-1-4398-1782-7 Vol. 1, 2009

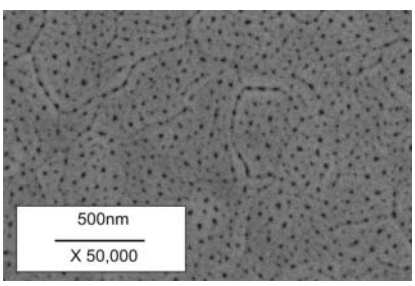
Test number	Voltage (V)	Temperature (˚C)	Time (minute)	Oxalic acid Concemtration (wt%)
1	40	25	5	0.3
2	40	15	20	1
3	40	0	60	3
4	50	25	20	3
5	50	15	60	0.3
6	50	0	5	1
7	60	25	60	1
8	60	15	5	3
9	60	0	20	0.3

Table 2: L_9 orthogonal array for Taguchi analysis

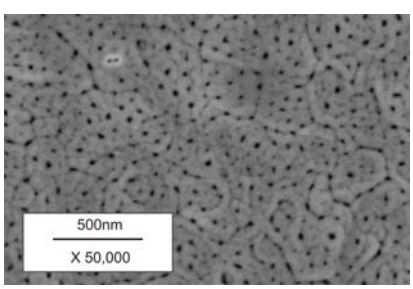
Various sections of the membrane were scanned at different magnifications in each case.

3 RESULTS AND DISCUSSION

Figure 2 depicts the effect of voltage on surface morphology for samples anodized in 3% oxalic acid, 10˚C, and 10 minutes. The average pore diameter during anodizing at 40 V is 16±3 nm and the pore density is 880 pore/μm^2 (Figure 2(a)). During anodizing at 60 V, with other conditions kept constant, the average of pore diameter was 26±5 nm, and the pore density is 400 pore/μm^2 (Figure 2(b)). It means that increase of voltage increases the pore diameter while it decreases their density. This general effect of voltage is in agreement with prior results [6, 29]. Although it is not clear that in other different conditions the voltage effect has the same strength or not.



(a)



(b)

Figure 2: Effect of voltage on first step of anodizing of aluminum in 3 wt% oxalic acid, 10˚C, and 10 minutes in (a) 40, (b) 60 V.

Figure 3, shows same samples as Figure 2(b), after removing the first anodizing layer. It could be observed that bottom of pores is bigger than pores which come to surface after first anodizing (45±6 nm compared to 16±3 nm).

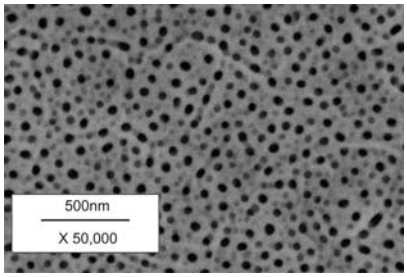


Figure 3: After removing the anodized layer fabricated in 3 wt% oxalic acid, 10˚C, 10 minutes and 60 V.

Figure 4 shows surface image after removing the alumina layer of sample anodized in 0.3 wt% oxalic acid, 10˚C, 60 V for 80 minutes. Comparing this image and Figure 3 shows that although the anodizing time for the sample in Figure 4 is greater than for the sample in Figure 3 (80 vs. 10 minutes), the pore density is much lower than it (320 vs. 480 pore/μm^2), due to 10 times lower electrolyte concentration. Also according to these images, pores are more uniform in the sample anodized in 3 wt% oxalic acid, while in the samples prepared in 0.3 wt% oxalic acid, big pores with average size of 50±7 nm coexist with pores as small as 25±7 nm.

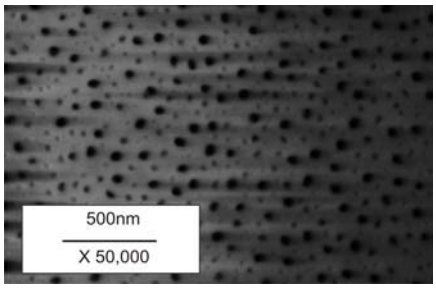


Figure 4: After removing the anodized layer fabricated in 0.3 wt% oxalic acid, 10˚C, 80 minutes and 60 V.

4 SUMMARY

Due to the importance of using tunable pore structure in nanoporous surfaces for various applications, the fabrication of nanoporous surfaces should be controllable. Anodizing the aluminum, which is a self assembly system, is an appropriate fabrication of nanoporous surface method for many applications. Anodized alumina can provide a wide range of pore structures. Knowing the governing rules in anodizing process will help to obtain the desirable structure. The effect of voltage, concentration and their interaction were studied. In order to reduce the number of experimental runs required to identify controlling variables, the Taguchi method was adopted.

5 REFERENCES

[1] L. Zhang, H.S. Cho, F. Li, R.M. Metzger, and W.D. Doyle, Journal of Materials Science Letters, 17(4), 291-294, 1998.

[2] S. Prasad, X. Zhang, C.S. Ozkan, and M. Ozkan, Electrophoresis, 25 (21-22), 3746-3760, 2004.

[3] S. Prasad, and J. Quiano, Biosensors and Bioelectronics, 21(7), 1219-1229, 2004.

[4] Reddy R.K.K. NanoMonitors: "Electrical Immunoassay for Clinical Diagnostics Implementation of a Microfabricated Biosensor for the Detection of Proteins," Master of Science Thesis, Portland State University, OR, 2007.

[5] M. Bothara, V. Venkatraman, R.K.K Reddy, T. Barrett, J. Carruthers, S. Prasad, Nanomedicine, 3(4), 423-436, 2008.

[6] A. Thormann, N. Teuscher, M. Pfannmöller, U. Rothe, A. Heilmann, Small, 3(6), 1032-1040, 2007.

[7] J.S. Chang, J.S. Hwang, S.H.W.A. Jhung, S.E. Park, G. Ferey, and A.K. Cheetham, Angewandte Chemie(International ed. Print), 43(21), 2819-2822, 2004.

[8] C. Xu, X. Xu, J. Su, and Y. Ding, Journal of Catalysis, 252(2), 243-248, 2007.

[9] J.J. Lee, S. Han, H. Kim, J.H. Koh, T. Hyeon, and S.H. Moon, Catalysis Today, 86(1-4), 141-149, 2003.

[10] K.C. Popat, E.E. Leary Swan, V. Mukhatyar, K.I. Chatvanichkul, G.K. Mor, C.A. Grimes, and T.A. Desai, Biomaterials, 6(22), 4516-4522, 2005.

[11] S.P. Adiga, L.A. Curtiss, J.W. Elam, M.J. Pellin, C.C. Shih, C.M. Shih, S.J. Lin, Y.Y. Su, S.D. Gittard, J. Zhang, et al, Journal of the Minerals, Metals and Materials Society, 60(3), 26-32, 2008.

[12] R. Etzioni, N. Urban, R. Scott, M. McIntoch, S. Schwatz, B. Reid, J. Radich, G. Anderson, and L. Hartwell, Nature Reviews/Cancer, 3, 243−252, 2003.

[13] X. Liu, Y. Won, and P.X. Ma, Biomaterials, 27(21), 3980-3987, 2006.

[14] K.M. Woo, V.J. Chen, and P.X. Ma, Journal of Biomedical Materials Research, 67(2), 531-537, 2003.

[15] I. Shishkovsky, Y. Morozov, and I. Smurov, Applied Surface Science, 254(4), 1145-1149, 2007.

[16] T.J. Webster, C. Ergun, R.H. Doremus, R.W. Siegel, and R. Bizios, Biomaterials, 21(17), 1803-1810, 2000.

[17] R.L. Price, K.M. Haberstroh, and T.J. Webster, Medical and Biological Engineering and Computing, 41(3), 372-375, 2003.

[18] T.J. Webster, M.C. Waid, J.L. McKenzie, R.L. Price, and J.U. Ejiofor, Nanotechnology, 15(1), 48-54, 2004.

[19] J. Zou, X. Qi, L. Tan, and B.J.H. Stadler, Applied Physics Letters, 89, 093106, 2006.

[20] M. Lahav, T. Sehayek, A. Vaskevich, and I. Rubinstein, Angewandte Chemie International Edition in English, 115(45), 5734-5737, 2003.

[21] N.W. Liu, A. Datta, C.Y. Liu, and Y.L. Wang, Applied Physics Letters, 82(8), 1281-1283, 2003.

[22] K. Nishio, T. Yanagishita, S. Hatakeyama, H. Maegawa, H. Masuda, The Journal of Vacuum Science and Technology B, 26(1), L10-L12, 2008.

[23] B.Y. Yoo, R.K. Hendricks, M. Ozkan, and N.V. Myung, Electrochimica Acta, 51(17), 3543-3550, 2006.

[24] H. Masuda and K. Fukuda, Science, 268(5216), 1466-1468, 1995.

[25] Y. Chen-Un, H. Chi-Chang, A. Bai, and Y. Yong-Feng, Surface & Coatings Technology, 201, 7259–7265, 2007.

[26] F. Li, L. Zhang, R.M. Metzger, Chemistry of Materials, 10, 2470-2480, 1998.

[27] P. J. Ross, "Taguchi Techniques for Quality Engineering," Mc-Graw-Hill, New York, 1989.

[28] D. C. Montgomery, "Design and Analysis of Experiments," 3rd Edition, Wiley, New York, 1991.

[29] F. Li, L. Zhang, R.M. Metzger, Chemistry of Materials, 10, 2470-2480, 1998.