

Ordered Nanoporous Alumina Membranes Formed in Oxalic/Phosphoric Acid Using Hard Anodization

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Abstract:

Highly self-ordered alumina nanopore arrays were fabricated using hard anodization technique in different mixtures of oxalic/phosphoric acid. The phosphoric acid concentration was varied from 0.05 to 0.3 M while the oxalic acid concentration was changed between 0.3 and 0.4 M. The self ordered nanoporous arrays were obtained in anodization voltage changing from 130 to 200 V. The interpore distances ranging from 270 to 500 nm were achieved. The interpore distance of the ordered samples was dependent upon the both anodization voltage and current density. The current density increased by increasing the anodization voltage that may be a reason to reduce the interpore distance from 2.2 V to 2.1 V. The best self ordered porous alumina oxide were obtained with 160, 165, and 185 anodization voltages, using different values of oxalic and phosphoric acid concentration. It was obtained that increasing the oxalic acid concentration in the electrolyte along with reducing the rate of anodization voltage controlled the hard anodization treatment such as better self ordered arrays.

Keywords: Anodization, porous material, scanning electron microscopy

1. INTRODUCTION

After introducing the two-step anodization technique under conventional so-called 'mild anodization' (MA) [1], anodized aluminum oxide (AAO) membrane has become one of the most common templates for preparation nanostructures such as nanowires, nanoparticles and nanotube [2-5] as well as nanocones and nanorings [6]. These AAO films are also widely used as filters [7] and two dimensional hexagonal photonic crystals [8]. The MA which is more conventional fabrication method was initially reported by Masuda and Fukuda [9]. This kind of anodization which is based on two-step process, takes tens hours of processing time and the self-ordering takes place only in a narrow range of

voltages. It is reported that long range ordering is possible if the applied potential and the pH value of the electrolyte, are adjusted so that the membrane porosity is 10 % [10]. Therefore, self ordered array is seen to occur under limited voltage conditions, takes place at 25 V in sulfuric acid [11], at 40 V in oxalic acid [12,13] and at 195 V in phosphoric acid solution [14] with an interpore distance of 63, 100, and 500 nm, respectively.

Using a mixture of phosphoric and oxalic acid, a perfect regularity was obtained at an anodization voltage of about 36 V [15]. Excellent self-ordered nanopore arrays with various porosities were also obtained at anodizing voltages of 25 and 40 V by the close control of pH and phosphoric/oxalic ratio [16].

Recently, a new method based on the hard anodization (HA) process was reported [17 -19] for fast fabrication of highly self-ordered AAO with a wide range of pore sizes and interpore distances for practical applications. In this new method, in a controllable procedure, an excellent array of nonporous was obtained applying a high current density for a relatively short time. It was found that highly self-ordered AAO films can be formed in a sulfuric acid solution under high electric fields near the breakdown potentials [17]. It was also reported that the nanopore arrays were fabricated with 240–300 nm interpore distances using a 0.3 M oxalic acid electrolyte and the best self-ordering was observed at an anodization voltage of 140 V [18]. The HA was also employed at the anodization voltage of 195 V using a mixture of phosphoric acid and ethanol at low temperature [19]. In our previous work, using hard anodization technique, the interpore distance was obtained from 130 to 270 nm which is useful in many applications from magnetic media to visible photonic crystals [20].

In this work, we report an approach for fabricating self-ordered AAO films using oxalic/phosphoric acid mixtures and anodization potentials over 100 V. The idea behind our efforts was to employ the HA technique using different electrolyte compositions with different acidities to optimize the anodizing potential having films with higher self-ordered arrays, controllable interpore distance. We extended the interpore distance to about 500 nm and a wide range of interpore distances and pore diameters were performed.

2. EXPERIMENTAL

High purity aluminum foil (99.999% purity, 0.3 mm thickness) was used as substrate, degreased in acetone, washed in deionized water. The native oxide layer was then removed using 3 M solution of NaOH for 3 min. The aluminum was then electropolished at a constant current density (100 mA/cm²) in a 1:4 volume mixture of perchloric acid and ethanol to diminish the roughness of the aluminum foil surface.

Hard anodization technique was employed using oxalic/phosphoric mixtures containing 0.3 and 0.4 M oxalic acid and x M phosphoric acid (x = 0.05, 0.1, 0.15, 0.2 and 0.3) as electrolyte. In each electrolyte mixture several samples were fabricated with different final anodization voltages. During the anodization process the electrolyte temperature of all the samples was kept constant at 0 °C. The conditions in which the samples were made are shown in tables 1, 2, 3 and 4.

To make a protective layer against high voltages in the hard anodization [15], the procedure was started with conventionally mild anodization at 35 V for 10 min. The anodization voltage was then increased to a final constant potential at a rate of 0.6 V/s and subsequently the anodization procedure was continued for an hour. The final voltages were selected relative to the voltage in which the current density was increased dramatically (this voltage was named threshold voltage and was abbreviated as V_{th}).

To investigate the morphology and ordering of holes of the samples in the end of HA, the SEM micrograph was prepared from underside of the holes after removing the thick layer of alumina.

3. RESULTS AND DISCUSSION

As it can be seen from table 1, five samples were fabricated with different oxalic/phosphoric mixtures. The oxalic and phosphoric acid concentrations were 0.3 and 0.05 M, respectively using different anodization voltages. For more information, the final anodization voltage, threshold voltage, a voltage in which the current density drastically changes (V_{th}), the current density at the end of anodization and the total anodization charge were tabulated. The final anodization voltages varied from 130 to 170 V. The experimental data in this table reveals that in an electrolyte with same composition and temperature, V_{th} is almost the same. This is an indication of excellent repeatability of the hard anodization technique in which the electrolyte temperature can be well controlled. On the other hand it was observed that electrolyte increased the threshold voltage to 115

Table 1: As-deposited conditions of the samples made in 0.3M/0.05M mixed oxalic/phosphoric acid.

Con. Oxalic Acid (M)	Con. Phosphoric Acid (M)	Final voltage (V)	Temp (°C)	Breaking voltage (V)	Max Current (mA)	Total Charge (C)
0.3	0.05	130	-1.5	116	248	39.4
0.3	0.05	140	-1.5	115	253	39.5
0.3	0.05	150	-1.5	115	233	45
0.3	0.05	160	-1.5	115	215	43
0.3	0.05	170	-1.5	117	235	42

Table 2: As-deposited conditions of the samples made in 0.3M/0.1M mixed oxalic/phosphoric acid.

Con. Oxalic Acid (M)	Con. Phosphoric Acid (M)	Final voltage (V)	Temp (°C)	Breaking voltage (V)	Max Current (mA)	Total Charge (C)
0.3	0.1	150	-1.5	150	-1.5	150
0.3	0.1	160	-1.5	149	-1.5	149
0.3	0.1	170	-1.5	153	-1.5	153
0.3	0.1	180	-1.5	150	-1.5	150

Table 3: As-deposited conditions of the samples made in 0.3M/0.2M mixed oxalic/ phosphoric acid.

Con. Oxalic Acid (M)	Con. Phosphoric Acid (M)	Final voltage (V)	Temp (°C)	Breaking voltage (V)	Max Current (mA)	Total Charge (C)
0.3	0.2	170	-1.5	168	243	32.8
0.3	0.2	180	-1.5	170	623	35.8

Table 4: Optimum conditions to fabricate the sample with larger domain size.

Con. Oxalic Acid (M)	Con. Phosphoric Acid (M)	Final voltage (V)	Temp (°C)	Breaking voltage (V)	Max Current (mA)	Total Charge (C)
0.4	0.1	160	+1	90	172	128
0.4	0.2	165	+1	111	210	124
0.4	0.25	185	+1	121	334	130
0.4	0.3	200	+1	130	350	128

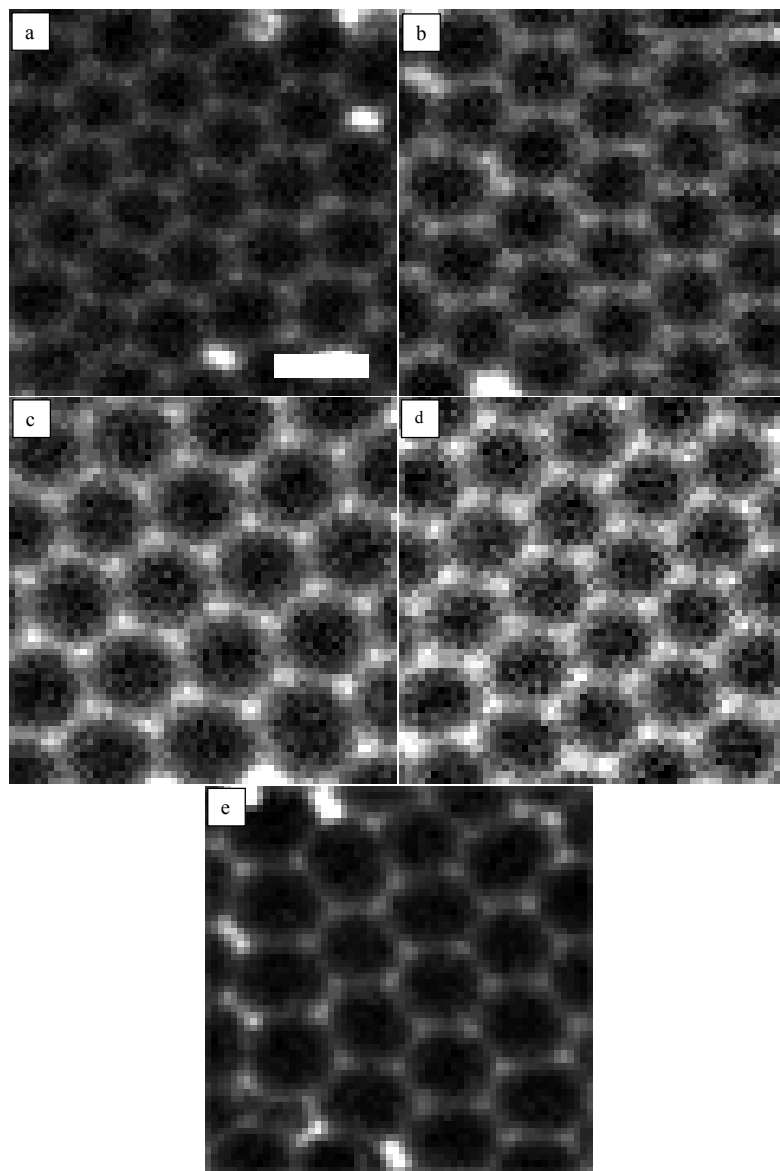


Figure 1: The SEM micrographs of nanohole configurations of samples made in oxalic/phosphoric mixture containing 0.3 M oxalic and 0.05 M phosphoric acid at anodization voltage of (a) 130 V, (b) 140 V, (c) 150 V, (d) 160 V, (e) 170 V. The scale bar is 500 nm.

V from 90 V by adding only 0.05 M phosphoric acid to a 0.3 M oxalic acid which was reported by Lee et al. [18]. They used pure oxalic acid as electrolyte and a 90 V threshold voltage were obtained. It may say that adding phosphoric acid to the oxalic acid enables us to control the hard anodization technique. Maximum anodization current densities and total anodization charges show a small standard deviation of 5% while by increasing the anodization

voltage to 140 V the total charge increases to about 10 % which represent a higher rate anodization for the higher anodization voltages.

Figures 1(a)–(e) show a 2.25 μm^2 SEM images of the AAO films fabricated under 130-170 V anodization voltages using 0.05 M phosphoric acid concentration. We can say that there is a wide region of the anodization voltage in which the

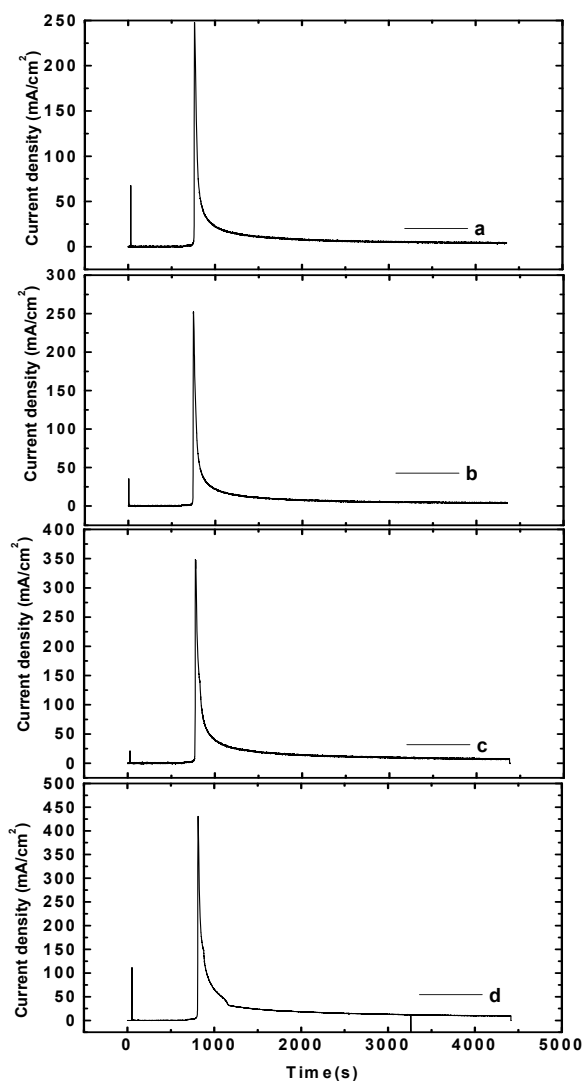


Figure 2: The current-time curves of the samples made in oxalic/phosphoric mixture containing 0.3 M oxalic and 0.05 M phosphoric acid at anodization voltage of (a) 130 V, (b) 140 V, (c) 150 V, (d) 160 V.

self-ordering take place. The interpore distance was evaluated from SEM images. As expected, increasing the anodization voltage increased the interpore distance but the ratio of the interpore distance to the anodization voltage was not the same for all the samples. In each sample this ratio reduced by increasing the anodization voltage. As evidence one can see that this ratio decreases from 2.2 to 2.1 nm/V for the SEM micrograph shown in Figure 1(a)

to that in Figure 1(e). For more information the final current at the end of anodization time and the total electrical charge is shown in table 1. The average interpore distances were measured to be about 270, 305, 325, 345 and 360 for the SEM micrographs seen in the Figures 1(a) to 1(e), respectively.

For more investigation, the measurement of the current density of all the samples as a function of time was performed. For this set samples current density-time curves are shown in Figure 2. The current density increased rapidly, reached a maximum and subsequently showed a nearly exponential decay as a function of time. As seen in this figure the peak intensity of the current density raises by increasing the anodization voltage. As mentioned earlier the total charge of the samples anodized with more than 140 V anodization voltage increased almost 10% which is a direct consequence of increasing the current density. As reported by Li et al. [19] there is an inverse relation between interpore distances and current density. This may be a reason to reduce the interpore distance from 2.2 V to 2.1 V when the anodization voltage increases from 130 V to 160 V, respectively.

Changing the concentration of the phosphoric acid to 0.1 M (see table 2) relatively reduced the ordered nanoporous arrays. The oxalic acid concentration of these set of samples was 0.3 M, same as previously samples and the anodization voltages varied from 150 V to 180 V. A relatively much difference was seen between two set of the samples. Although the anodization temperature for both sets of samples is the same, adding phosphoric acid molarity to 0.1 M from initially 0.05 M increased the threshold voltage to 150 V from primarily 115 V which is a sign of influence of electrolyte composition to the threshold voltage. The second interesting point is that increasing the final anodization voltage from 150 V to 180 V increased the current density from 170 to 611 mA/cm²; a 350% enhancement, while the standard deviation of current density for the first set of the samples was less than 1%. In contrast with current density, maximum enhancement of total charge was about 100% when the anodization voltage changed to 180 V from initially 150 V.

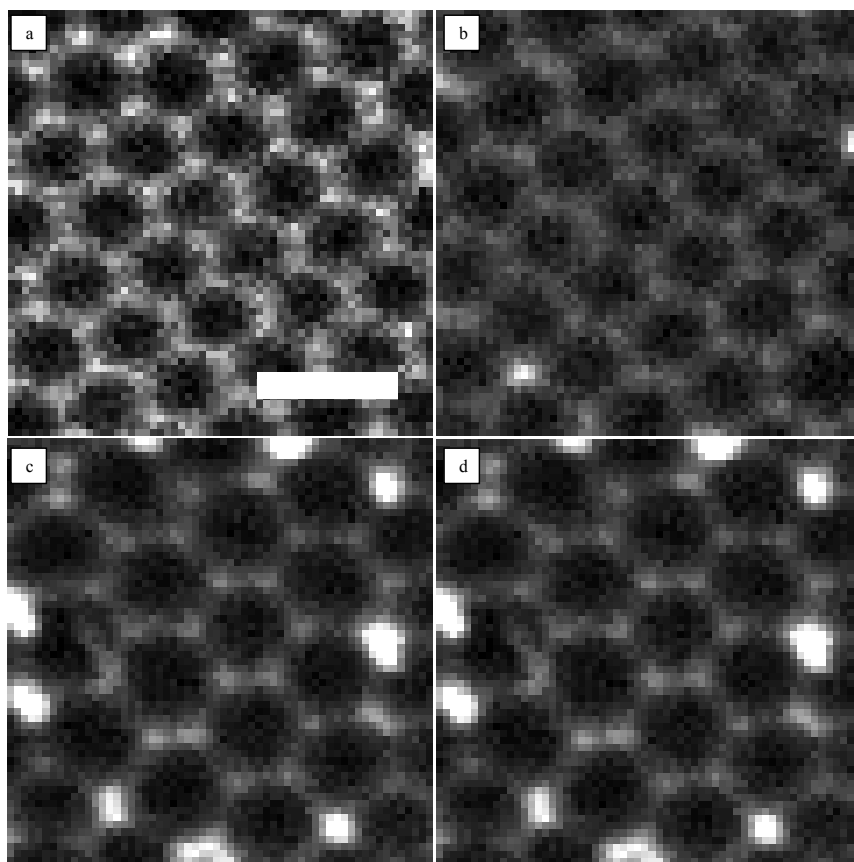


Figure 3: The SEM micrographs of nanohole configurations of samples made in oxalic/phosphoric mixture containing 0.3 M oxalic and 0.1 M phosphoric acid at anodization voltage of (a) 150 V, (b) 160 V, (c) 170 V, (d) 180 V. The scale bar is 500 nm

Figure 3 shows the SEM micrograph of this set of samples. As mentioned above the self ordering of this set of samples is less than that of the first one while it was expected that increasing the current density increases the self ordered arrays. For more investigation the current-voltage curves of these samples are shown in figure 4. According to these curves the inconsistency of maximum current density and total anodization charge values could be clarified. Although by increasing the anodization voltage, the maximum current density drastically increases but the rapid reduction of the current density after reaching to its maximum values may be a reason for this set of samples having less self ordering. High current density variations of these samples seem to prevent the self ordering and led to form two types of ordered arrays with various

interpore distances. Smaller interpore distances are related to the sharp increase of the current density which was not continued for a considerable period of time. It was seen that by increasing the anodization voltage, the current density increases thereby reduces the interpore distance. For this set samples, the inter pore distances were found to be about 317, 340, 360 and 375 nm for the samples fabricated with anodization voltage of 150 V, 160 V, 170 V and 180 V, respectively. To extend our study on the hard anodization technique and in order to obtain different interpore distances phosphoric concentration in the mixture increased to 0.2, 0.3 and 0.3 M. Herein the only two samples made in 0.3/0.2 M oxalic/phosphoric mixture are highlighted. The current density of these samples is seen in Figure 5. Table 3 indicates more details of these samples.

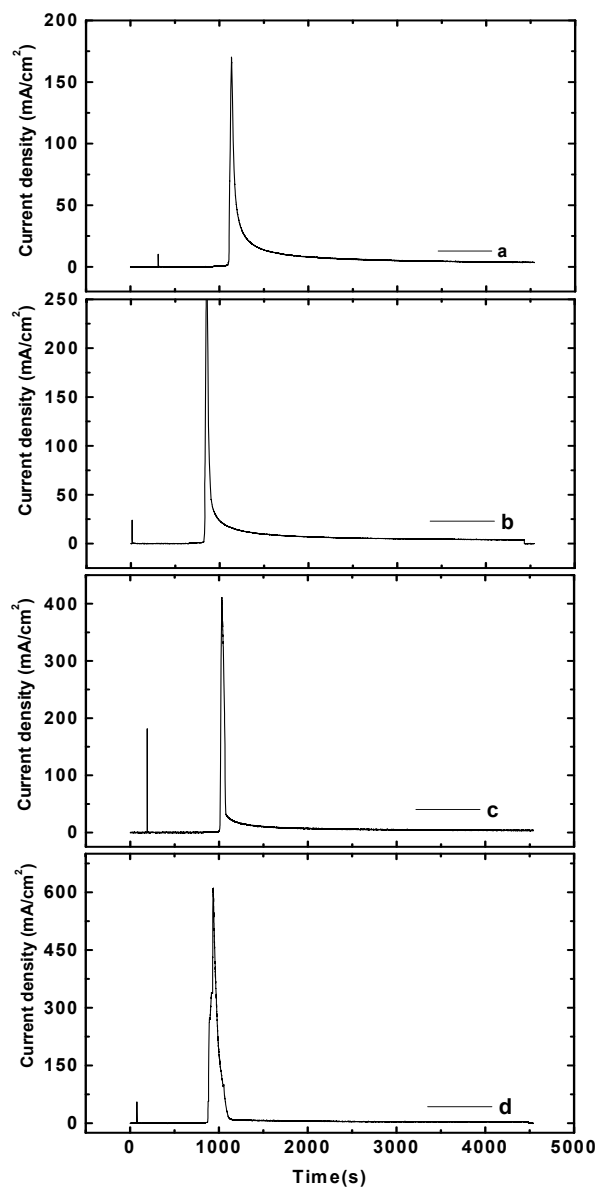


Figure 4: The current-time curves of the samples made in oxalic/phosphoric mixture containing 0.3 M oxalic and 0.1 M phosphoric acid at anodization voltage of (a) 150 V, (b) 160 V, (c) 170 V and (d) 180 V.

As it can be seen from this table, the treatment of these samples are same as the second set and self ordered arrays with large domain size was not expected. The SEM micrographs of these samples are also provided (see Figure 6). It is seen that the interpore distance was increased by increasing the anodization voltage.

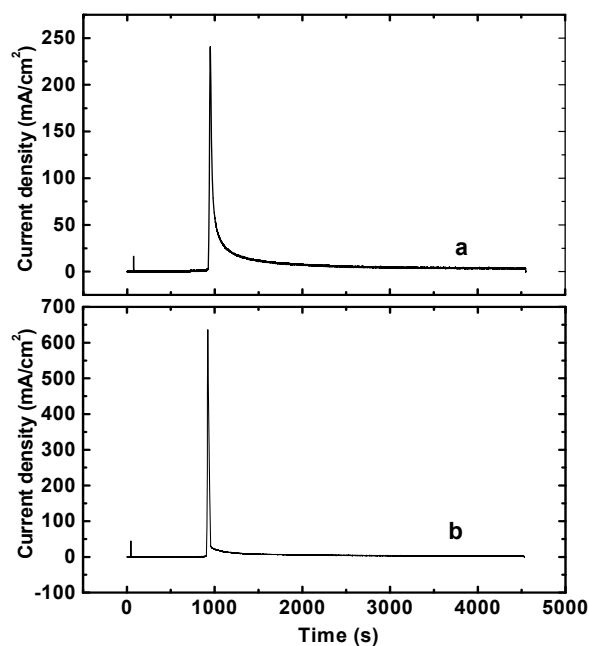


Figure 5: The current-time curves of the samples made in oxalic/phosphoric mixture containing 0.3 M oxalic and 0.2 M phosphoric acid at anodization voltage of (a) 170 and (b) 180 V

To solve this problem, fabricating the films with highly ordered nanoporous having one domain size following considerations was performed. According to Lee et al.[18] the oxalic concentration has a dominant role on the self ordered nanopore arrays in the hard anodization technique. Therefore, in the present work an electrolyte with relatively high oxalic concentration was performed. On the other hand, in order to reduce the threshold voltage the rate of the increasing the anodization voltage was reduced. This led the system to better sense of the increasing of the anodization voltage thereby perform faster reaction and decreases the threshold voltage. Higher oxalic acid concentration along with reduction in the threshold voltage reduced the maximum anodization current density thereby self ordered arrays with larger domain sizes were formed.

Using this method and applying different electrolyte acidities and voltages, the optimum conditions were found and are tabulated in table 4. As evidence the current density-time curves of the best self-ordered samples (made with 160, 165, 185 and 200 V, anodization voltage) are presented in Figure 7. It

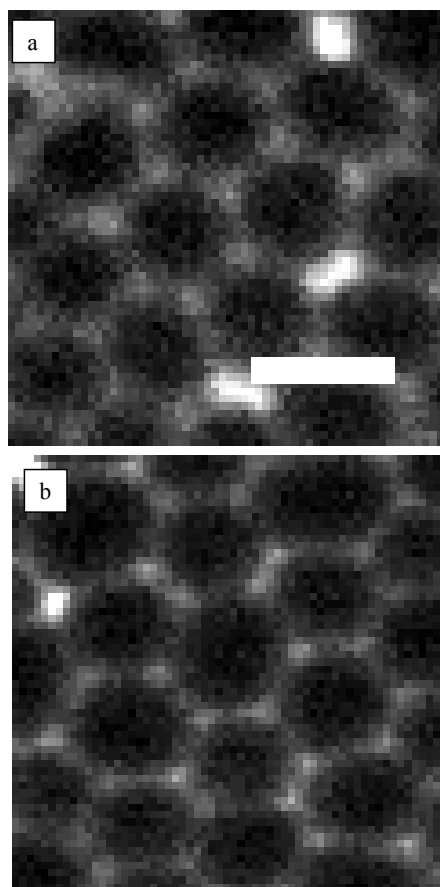


Figure 6: The SEM micrographs of nanohole configurations of samples made in oxalic/phosphoric mixture containing 0.3 M oxalic and 0.2 M phosphoric acid at anodization voltage of (a) 170 V and (b) 180 V. The scale bar is 500 nm.

can be observed that the self-ordering anodization voltage is a region corresponds to the points on the current-time curve located between two peaks of current density-time curve.

Since the interpore distance is not only dependent on the anodizing voltage but is also influenced by the anodizing current density for a certain electrolyte composition, it was expected that the ratio of the interpore distance to the anodization voltage decreases by increasing the anodization voltage. Figure 8 shows SEM images ($4 \mu\text{m}^2$) of the AAO films fabricated under 160, 165, 185 and 200 V anodization voltages, using different values of

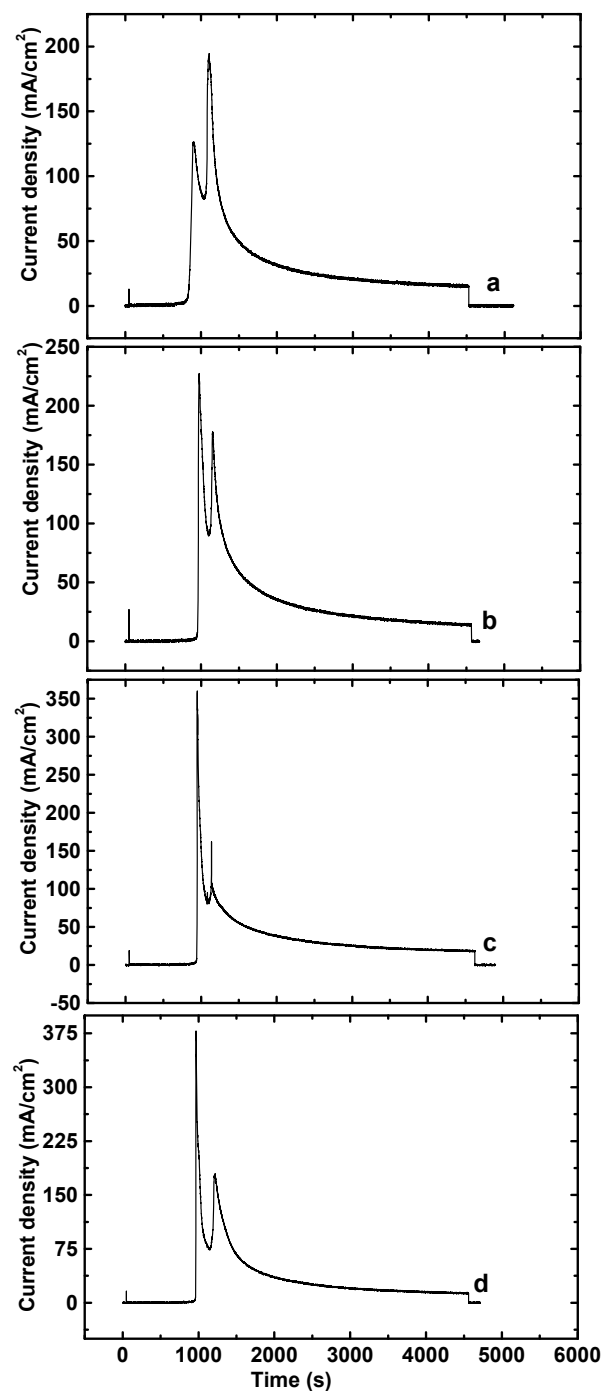


Figure 7: The current-time curves of the samples made in oxalic/phosphoric mixture containing 0.4 M oxalic and 0.2, 0.1 and 0.1 M phosphoric acid at anodization voltage of (a) 160, (b) 165, (c) 185 and (d) 200 V, respectively.

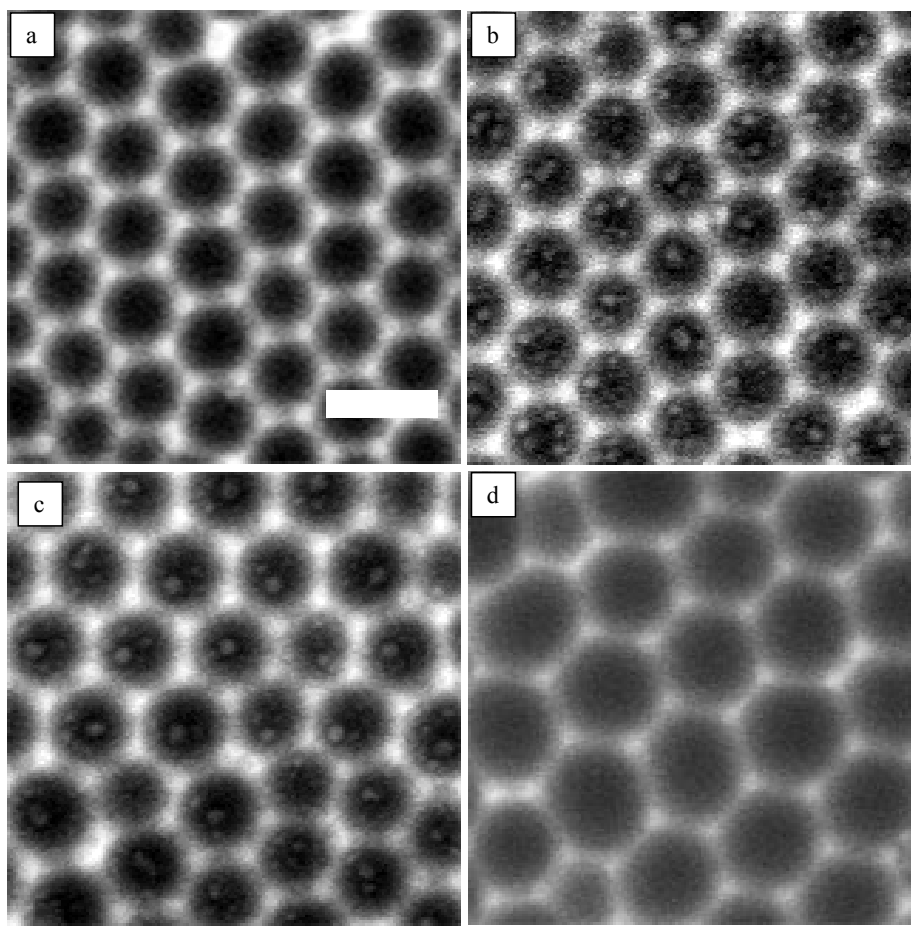


Figure 8: The SEM micrographs of nanohole configurations of samples made at different oxalic/phosphoric mixture concentrations at anodization voltage of (a) 160 V, (b) 165 (c) 185 V and (d) 200 V. The scale bar is 500 nm.

oxalic and phosphoric acid concentration as shown in table 4. As seen in this figures, almost all the samples are self-ordered within a relatively large domain. Increasing the anodization voltages to 200 V disturbed the self ordering and more than one type of pore with different pore sizes was observed.

4. CONCLUSIONS

The ordering of porous alumina nanoholes fabricated by hard anodization technique in phosphoric/oxalic mixtures with a wide range of phosphoric acid concentrations and anodization voltages were studied. Our investigations on the effect of anodization voltage and phosphoric concentration

on the ordering, interpore distances enables us to achieve the following conclusions:

1. Adding phosphoric acid to oxalic acid electrolyte using hard anodization technique enables us to obtain self ordered arrays in a wide range of anodization voltage.
2. High phosphoric acid concentration increased the both threshold voltage and current density of the samples thereby reduced the self ordered domain size.
3. Increasing the oxalic acid concentration in the electrolyte along with reducing the rate of anodization voltage controlled the hard anodization treatment such as self ordered arrays.

REFERENCES:

1. H. Masuda, A. Fukuda, *Science* 268 (1995) 1466.
2. J. Qin, J. Nogues, M. Mikhaylova, A. Roig, J. S. Munoz, M. Muhammed, *Chem. Mater.* 17 (2005) 1829.
3. S. Zhao, L. Clime, K. Chan, F. Normandin, H. Roberge, A. Yelon, R. W. Cochrane, T. Veres, *J. Nanosci. Nanotechnol.* 7 (2007) 381.
4. M. Lahav, E. A. Weiss, Q. Xu, G. M. Whitesides, *Nano Lett.* 6 (2006) 2166.
5. H. Masuda, K. Yasui, K. Nishio, *Adv. Mater.* 12 (2000) 1031.
6. S. Zhao, H. Roberge, A. Yelon, T. Veres, *J. Am. Chem. Soc.* 128 (2006) 12352.
7. T. Kyotani, W. H. Xu, Y. Yokoyama, J. Inahara, H. Touhara, A. Tomita, *J. Membr. Sci.* 196 (2002) 231.
8. H. Masuda, M. Ohya, K. Nishio, H. Asoh, M. Nakao, M. Nohtomi, A. Yokoo, T. amamura, *Jpn. J. Appl. Phys.* 39 (2000) L1039.
9. H. Masuda, K. Fukuda, *Science* 268 (1995) 466.
10. K. Nielsch, J. Choi, K. Schwirn, R. B. Wehrspohn, U. Gosele, *Nano Lett* 2 (2002) 677.
11. H. Masuda, F. Hasegawa, S. Ono, *J Electrochem Soc* 144 (1997) L127.
12. A.P. Li, F. Muller, A. Birner, K. Nielsch, U. Gosele *J Appl Phys* 84 (1998) 6023.
13. M. Almasi Kashi, A. Ramazani *J Phys D: Appl Phys* 38 (2005) 2396.
14. H. Masuda, K. Yada, A. Osaka *Jpn J Appl Phys* 37 (1998) L1340.
15. S. Shingubara, K. Morimoto, H. Sakaue, T. Takahagi, *Electrochem. Solid-State Lett.* 7 (2004) E15.
16. M. Almasi Kashi, A. Ramazani, M. Rahmandoust, M. Noormohammadi *J. Phys. D: Appl. Phys.* 40 (2007) 4625.
17. S. Z. Chu, K. Wada, S. Inoue, M. Isogai, A. Yasumori, *Adv. Mater.* 17 (2005) 2115.
18. W. Lee, R. Ji, U. Gosele, K. Nielsch, *Nature Mater.* 5, (2006) 741.
19. Y Li, M Zheng, L Ma, W Shen, *Nanotechnology* 17 (2006) 5101.
20. M. Almasi Kashi, A. Ramazani, M. Noormohammadi M. Zarei, P. Marashi *J. Phys. D: Appl. Phys.* *J Phys D: Appl Phys* 40 (2007)7032.