

NANO LETTERS

Self-ordering Regimes of Porous Alumina: The 10% Porosity Rule

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Received February 28, 2002; Revised Manuscript Received April 29, 2002

ABSTRACT

Transmission electron microscopy analysis of self-ordered porous alumina obtained by electrochemical anodization shows that self-ordering requires a porosity of 10%, independent of the specific anodization conditions. This corresponds to a volume expansion of alumina to aluminum of about 1.2. We propose that self-ordering of porous alumina with any interpore distance is possible if the applied potential, which mainly determines the interpore distance, and the pH value of the electrolyte, which mainly defines the pore radius, match the 10% porosity rule.

The formation of disordered porous alumina by the anodization of aluminum has been widely studied to protect and decorate the surface of aluminum and to make inorganic membranes.¹ Since Masuda et al. reported the two-step anodization process to obtain self-ordered alumina structures in 1995,² new areas of applications have emerged in the fields of magnetic storage,³ solar cells,⁴ carbon nanotubes,⁵ catalysts,⁶ and metal nanowires.^{7–8} This increasing attraction of porous alumina as template is mainly due to its relatively easy and low-cost processing. To date, it is possible to fabricate well-defined self-ordered porous alumina with 50, 60, 100, 420, and 500 nm interpore distance.⁹ Alumina templates with interpore distances between 100 and 420 nm might be achieved via pre patterning methods such as imprint lithography or e-beam lithography.^{10,11} However, lithographic methods are very cost and time intensive and are not necessary for a variety of template applications. Therefore,

it would be extremely beneficial to obtain a general rule to obtain self-ordered pores with any lattice constant.

The arrangement and shape of alumina pores are determined by the applied voltage, temperature, and type and concentration of the electrolyte. For instance, if special self-ordering conditions are used to anodize the aluminum, hexagonally arranged arrays with circular pores can be obtained (Table 1). Here, we define self-ordered to be when more than the nearest neighbor is arranged hexagonally as determined by the radial distribution function.⁹

Experimental details of the fabrication of highly ordered alumina pore arrays have been reported elsewhere.^{9,12,13} After anodization, the total amount of Al ions was estimated by measuring the aluminum concentrations in the electrolyte Al_{aq}^{3+} with atomic absorption spectroscopy. By relating this value to the total amount of oxidized aluminum atoms that are calculated from the charge flow during the anodization ($Al_{tot} = 1/3 \int I dt$), we estimated the amount of alumina $W_{AlOx}/W_{Al} = (1 - Al_{aq}^{3+}/Al_{tot})$ with W_{Al} the weight of aluminum,

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Table 1: Results of Structural Property of Self-ordered Porous Alumina Analyzed from TEM Images in Figure 1^a

electrolyte	interpore distance D_{int}	inner wall thickness D_{inner}	pore diameter $D_p (= 2r)$	porosity P	pK_s
H ₂ SO ₄ 25 V, 0.3 M	66.3 nm	7.2 nm	24 nm	12%	0.1
(COOH) ₂ 40 V, 0.3 M	105 nm	9.1 nm	31 nm	8%	1.125
H ₃ PO ₄ 195 V, 0.1 M	501 nm	54 nm	158.4 nm	9%	2.1

^aNote that the porosity of alumina is always about 10%.

W_{AlOx} the weight of alumina. The volume expansion ξ is determined by

$$\xi = \frac{V_{\text{AlOx}}}{V_{\text{Al}}} = \frac{W_{\text{AlOx}}}{W_{\text{Al}}} \times \frac{\rho_{\text{Al}}}{F_w \times \rho_{\text{AlOx}}} \quad (1)$$

where ρ_{Al} is the density of aluminum (2.7 g/cm³), ρ_{AlOx} the density of porous alumina (3.2 g/cm³, measured value), and F_w the weight fraction of aluminum ions in alumina ($F_w = 0.53$). The density of porous alumina was estimated by the floating method using thallos formate–malonate/H₂O mixtures.

We have analyzed in detail the cell structure of the self-ordered porous alumina by transmission electron microscopy (TEM). Figure 1 (a–c) shows TEM images of porous alumina with well-arranged arrays anodized in H₂SO₄, (COOH)₂, and H₃PO₄, respectively. At first glance, neglecting the scale, all three TEM pictures look similar. Indeed, analysis of the pictures yields a constant ratio of the radius of the pores r to the interpore spacing D_{int} (Table 1). Moreover, the walls between pores consist of a dark inner layer, far from the pore, and relatively bright outer layer. Numerical analysis of Figure 1 shows that the ratios are for all self-ordered regimes constant of about $D_{\text{inner}}/D_{\text{outer}} = 0.2 \pm 0.02$ (Table 1).

It has been reported by Thompson et al.¹⁴ that the outer layer is anion-contaminated, whereas the inner layer consists of a dense pure alumina. This explains the different contrast in TEM. Interestingly, Thompson et al. found that the ratio of the inner to outer layer strongly depends on the acid. For example, $D_{\text{inner}}/D_{\text{outer}} = 0.05$ for H₂SO₄, 0.1 for (COOH)₂, and 0.5 for H₃PO₄.¹⁵ However, they had concentrated their work on disordered pore regimes. In the case of a well-defined self-ordered porous alumina, we observe always the same r/D_{int} as well as the same $D_{\text{inner}}/D_{\text{outer}}$. The porosity of a hexagonal structure is given by

$$P = \frac{2\pi}{\sqrt{3}} \left(\frac{r}{D_{\text{int}}} \right)^2 \quad (2)$$

Since r/D_{int} is constant for self-ordered porous alumina, the optimum porosity is around 10% (Table 1). Note that the slightly larger pore diameter of the H₂SO₄ sample is due to chemical attack of the pore walls. Note that in the disordered growth regime, the porosity can be significantly larger or even smaller than 10%.¹⁶ For example, using 160 V instead of 195 V in 0.1 M H₃PO₄, the porosity is about 40%.

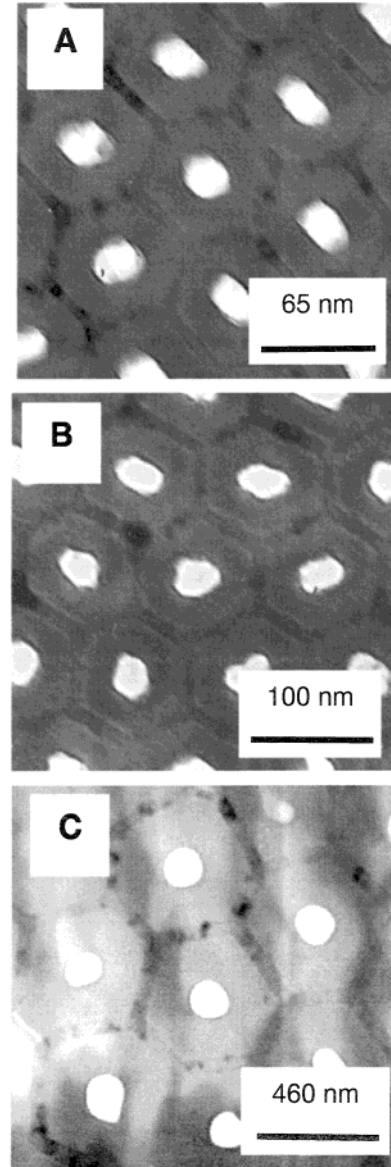


Figure 1. Transmission electron micrographs of self-ordered porous alumina fabricated at (a) 25 V in 1.7 wt % H₂SO₄, (b) 40 V in 2.7 wt % (COOH)₂, and (c) 195 V in 1 wt % H₃PO₄.

It is well known for alumina that the interpore distance, D_{int} , is linearly proportional to the applied cell potential U with a proportionality constant k of approximately $k \approx 2.5$ nm/V

$$D_{\text{int}} = kU \quad (3)$$

where under optimum conditions $D_{\text{int}} \approx 2D_{\text{B}}$, where D_{B} is the thickness of the barrier. This condition guarantees that no new pores nucleate between existing pores. This is similar to macroporous *p*-type silicon where the wall thickness is twice the depletion width.¹⁷ Therefore, the interpore distance and barrier-oxide thickness are determined solely by the applied potential. On the other hand, it is reported that the pore diameter, $2r$, is affected strongly by dissolution velocity of alumina that is determined by the pH value in the solution.¹⁸ The lower the pH, the lower the potential threshold for field-enhanced dissolution at the pore tip. Depending on the potential, the shape and the diameter of the pore are defined similar to mesopores in silicon.¹⁹ The smallest pores can be obtained in the lowest pH value, i.e., in the strongest acid. For example, for a pH of 1.09 in H_2SO_4 , the diameter $2r$ is 24 nm (Table 1). From our experimental observations of the 10% porosity rule, eq 3 can be written for self-ordered pore growth as

$$U = \sqrt{\frac{2\pi}{\sqrt{3}P}} \frac{r}{k} \quad (4)$$

where, under optimum self-ordering conditions, $P = 10\%$. From eq 4, the required potential, U , to obtain self-ordered alumina growths for a given pore radius, i.e., pH value, can be calculated. As a matter of fact, H_2SO_4 , $(\text{COOH})_2$, and H_3PO_4 have different pH values. Therefore, we obtain different self-ordering regimes for different potentials (eq 4). Moreover, changing the concentration would also lead to a change of the pH value. Indeed, increasing the concentration by a factor of 10, leads to a 20% decrease in the optimum interpore distance. For example, increasing from 1 to 10 wt % H_2SO_4 leads to a reduction of the lattice constant from 65 to 50 nm.^{9,10} A similar relationship is also observed for H_3PO_4 .¹³

Beyond the local matching of the 10% porosity rule for a one-unit cell as analyzed by TEM, also global matching must occur. Indeed, numerical image treatment of the sample surface has shown that for the ordered pore regimes (Table 1) the areal pore nucleation density corresponds to the optimum pore nucleation density n given by $n = 2k^{-2}U^{-2}/\sqrt{3}$.

The observation of the 10% porosity rule strongly supports our previously proposed mechanical stress model.^{12,13} It was proposed that in addition to the short-range order determined by eq 3, a force promoting medium range order must exist. In contrast to macroporous silicon, porous alumina consists of two different materials: an aluminum substrate and a porous alumina layer. When aluminum is anodized to alumina, there is a significant volume expansion ξ , which leads to mechanical stress in the thin alumina layer. For nonporous layers, the stress is maximal ($\xi_{\text{max}} \sim 2$) and it will decrease with porosity. As shown by Jessensky et al., if $\xi < 1.2$, i.e., the initial porosity is large, the force promoting ordering is too small and the pore array remains disordered. If $\xi \approx 1.2$, there is a small force promoting ordered pore growth. If $1.3 < \xi < \xi_{\text{max}}$, the size of the domains will decrease and finally disappear. We have shown

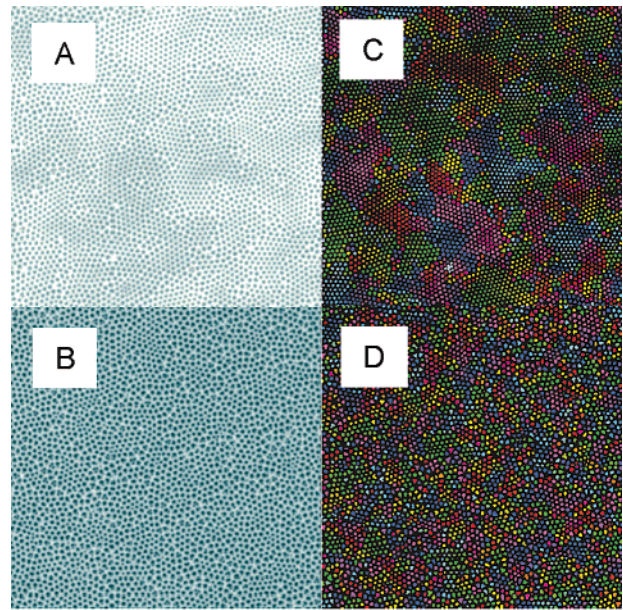


Figure 2. Scanning electron micrographs from phosphoric acid samples anodized for 24 h (A) and 48 h (B) in 1 wt % H_3PO_4 at 195 V, resulting in 500 nm interpore distance. C and D: Numerical image treatment of A and B, respectively, showing the domain size in false colors.

that $P = 10\%$ will lead to optimally ordered pore growth. We measured the ratio $W_{\text{AlOx}}/W_{\text{Al}}$ by analyzing the amount of Al^{3+} ions in the solution after anodization by atomic absorption spectroscopy. In the case of self-ordered alumina, 23% Al^{3+} ions are detected in the solution, taking into account that each aluminum atom needed three charges to dissolve. Thus, the self-ordered alumina maintains 77% of Al^{3+} ions, which corresponds to a volume expansion by a factor of 1.23 (eq 1). This is in good agreement with the values of Jessenky et al. obtained from gravimetric measurements.¹² Also, it is in line with results obtained by Li et al. who performed thickness measurements assuming 10% porosity of porous alumina.¹³

From these findings, it can be expected that after long anodization times in the ordered regime the 10% porosity rule cannot be maintained, when the conditions at the pore bottom will change due to diffusion limitations. Figure 2 shows two SEM images of porous alumina obtained by anodization in H_3PO_4 after 24 h (a) and 48 h (b). Numerical image treatment (Figure 2c,d) of these pictures shows that the size of the ordered domains (false colors) decreases with anodization time. Analysis of a series of porous alumina structures shows that the domain size does not linearly increase with time but has a maximum (Figure 3). The reason the domain size decreased after a critical time can be explained as an aberration from the 10% porosity rule due to a change of the pH value at the pore tip. In addition, we observed that the shape of pores after long anodization is not any more a circle as it is observed in the ordering regimes but a triangle or a polygon. Current transients show that the current increases again after a critical time, implying the change of conditions at the tip (Figure 3). These results suggest that there is an optimum anodization time to obtain the largest domain size. This goes beyond the results of Li

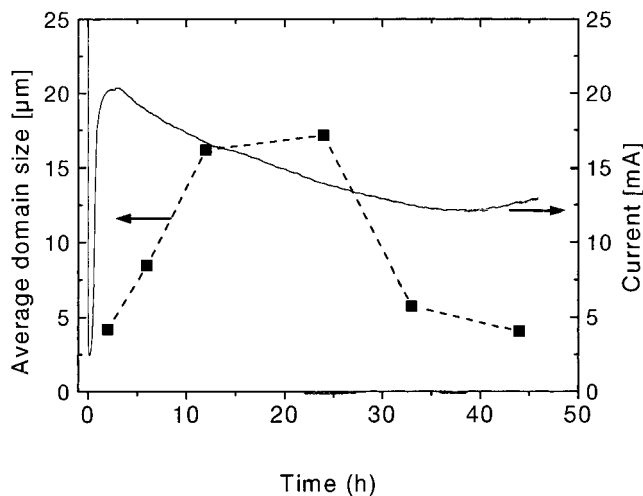


Figure 3. (left axis) Average domain size as a function of the anodization time during anodization in 1 wt % H_3PO_4 at 195V. The domain size is obtained by numerical picture treatment. First the domain size increases due to self-ordering, but after a critical time shown by the dashed line the domain size decreases again. (right axis) Current transient during of the same sample, showing first a current decrease typical for self-ordering, and then after a critical time the current increases.

et al. who reported that the average domain area is a linear function of anodization time.²⁰

In summary, we have presented a TEM analysis of self-ordered porous alumina obtained by electrochemical anodization. We find that self-ordering of porous alumina requires a porosity of 10%, independent of the specific anodization conditions. This corresponds to a volume expansion of alumina to aluminum of about 1.2. Therefore, to obtain self-ordered porous alumina for a given interpore distance, the applied potential, which mainly determines the interpore distance, and the pH value of the electrolyte, which mainly defines the pore radius, should match to fulfill the 10% porosity rule. Based on the 10% porosity rule, we were able to explain the deviations of ordered growth after long time anodization in terms of a change of the pH value at the pore tip.

Acknowledgment. The authors thank W. Erfurth, U. Doss, and S. Hopfe for technical support and F. Müller for stimulating discussion and numerical support.

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NL025537K