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Nanoporous anodic aluminum oxide with a long-range order and tunable cell sizes by phosphoric acid anodization on pre-patterned substrates

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Abstract

Nanoporous anodic aluminum oxide (AAO) has been explored for various applications due to its regular cell arrangement and relatively easy fabrication processes. However, conventional two-step anodization based on self-organization only allows the fabrication of a few discrete cell sizes and formation of small domains of hexagonally packed pores. Recent efforts to pre-pattern aluminum followed with anodization significantly improve the regularity and available pore geometries in AAO, while systematic study of the anodization condition, especially the impact of acid composition on pore formation guided by nanoindentation is still lacking. In this work, we pre-patterned aluminium thin films using ordered monolayers of silica beads and formed porous AAO in a single-step anodization in phosphoric acid. Controllable cell sizes ranging from 280 nm to 760 nm were obtained, matching the diameters of the silica nanobead molds used. This range of cell size is significantly greater than what has been reported for AAO formed in phosphoric acid in the literature. In addition, the relationships between the acid concentration, cell size, pore size, anodization voltage and film growth rate were studied quantitatively. The results are consistent with the theory of oxide formation through an electrochemical reaction. Not only does this study provide useful operational conditions of nanoindentation induced anodization in phosphoric acid, it also generates significant information for fundamental understanding of AAO formation.

Keywords

Anodic aluminum oxide; Phosphoric acid; Anodization; Imprinting; Silica nanobeads

1. Introduction

Owing to its self-ordered pore arrangement, straight through-pore geometries and ready availability out of a clean room environment, nanoporous anodic aluminum oxide (AAO) is attractive to numerous applications such as electrical and optical sensing, separating molecules and particles, as well as templating various nanostructures [1–10]. Conventionally, AAO films with self-ordered nanoporous structures are fabricated following a two-step anodization process developed by Masuda *et al* [10–12]. Although various anodization parameters have been studied in great detail, only a few discrete cell sizes are

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available using the self-ordering method. These are determined mainly by the applied voltage and type of acids used: for example, sulfuric acid at 25 V, oxalic acid at 40 V and phosphoric acid at 195 V give 63 nm, 100 nm and 500 nm pore intervals, respectively [13]. When an anodization of aluminum is carried out outside of these narrow process windows, the degree of spatial organization decreases considerably. Another shortcoming of the self-ordering method is the need of long anodization time and a relatively thick aluminum layer. Thus, the method does not apply easily to aluminum thin films deposited on a substrate [14]. Furthermore, the domain size with hexagonal packed pores is limited to several micrometers; it is difficult to obtain long range order through the self-organization process.

As an alternative to the self-ordered anodization, pre-patterning techniques to modify an aluminum surface prior to anodization have been introduced to improve a long-range order of AAO cell array, promote tunable cell sizes, reduce the anodization time and enable straight pores in thin aluminum films on different substrates. The indented topographic features produce a high local electric field, which enhances dissolution of the oxide film and serve as pore nucleation sites [15]. Shallow indentations have been created from various molds. For example, Masuda *et al.* used a SiC mold containing hexagonal array of convexes created by e-beam lithography to produce highly ordered AAO films [16]. Mikulskas *et al.* used an optical diffraction grating as an imprinting mold to pattern an aluminum surface [17]. However, the small dimension and high cost of the fabricated molds limit their wide applications. Alternatively, focused ion beam drilling has been used to indent aluminum directly [18, 19], while the patterned area is limited to the 10–100 μm order due to the slow and serial indentation process. Various approaches to pattern a large area of aluminum for ordered AAO have been reported. Ordered arrays of nickel bumps or pyramids have been created by interference lithography and used as a stamping mold for wafer-scale anodization [20]. Holographic lithography has also been employed to create photoresist grating patterns on a thin film aluminum and form highly ordered AAO [21]. Recently, a combination of imprinting lithography and wet etching has been carried out to grow highly ordered AAO on a 4-in silicon wafer [22]. However, these nano-lithographic patterning techniques require sophisticated clean room facilities and are not easily accessible. On the other hand, several groups have utilized nanobeads of 13–500 nm in diameter to imprint an aluminum surface and guide highly ordered pores in AAO [23, 24]. The nanobead molds offer an advantage over other imprinting methods in that no clean room access is required and continuously tunable bead sizes are easily available [23–25]. Moreover, nanobeads can be patterned into long range hexagonally ordered domains in scalable processes [26], enabling large area AAO formation through pre-patterning.

Despite numerous reports on pre-patterning guided anodization, prior work has focused on pattern transfer from the mold to the oxide film; there is little knowledge about how the electrolyte composition affects the oxide formation. Additionally, cell size of ordered AAO is limited to below 500nm, even with the nanoindentation approach. To address these limitations, we report here an investigation of oxide film growth rate as a function of acid concentration for cell sizes in a wide range through pre-patterned aluminum anodization in phosphoric acid. We use monolayers of hexagonally packed silica nanobeads as the imprinting mold to control the cell size between 280 to 760 nm. In addition to the acid concentration, the relationships between cell size, intrinsic pore size, anodization voltage and oxide film growth rate are also studied quantitatively.

2. Experimental details

2.1. Overview of the strategy to form tunable AAO pores through nanoimprinting

The schematic in Fig. 1 demonstrates the process to fabricate highly ordered nanoporous AAO thin films by nanobead imprinting. The process starts from depositing silica

nanoparticles into a large, continuous and close-packing monolayer on glass slides by the convective deposition [27] (Fig. 1(a)–(b)). Polystyrene nanobeads are mixed into the suspension at a concentration of 4 vol%, co-deposited and melted afterwards to stabilize the silica monolayer. The silica monolayer is then used as a template mold to imprint an aluminum thin film (Fig. 1(c)–(d)). The resulting nanodimple arrays on the aluminum surface (Fig. 1(e)–(f)) serve as pore nucleation sites in subsequent anodization and guide the formation of straight pores of the desired pore size in phosphoric acid under a constant voltage (Fig. 1(g)–(h)).

2.2. Creation of the nanoimprinting mold

Monodispersed silica nanobeads were synthesized by hydrolysis of tetraethyl orthosilicate (TEOS) (Sigma-Aldrich, Cat# 131903) following a recipe modified from the literature [25]. Deionized (DI) water, ethanol (Pharmco-AAPER, 200 Proof), NH_4OH (Fisher Scientific, Cat# A669-500) and TEOS were mixed at different ratios (Table S1) and left to react at room temperature for 24 hours under continuous stirring. The synthesized silica nanobeads were in the range of 280 nm to 760 nm with a narrow size distribution. After multiple washes by DI water and concentration by centrifugation, suspensions of the nanobeads were diluted to 16 vol% in DI water. Close-packed silica-nanobead monolayers were prepared through convective deposition on plain glass slides following the method reported by Kumnorkaew [27]. The deposition blade, a parafilm treated glass slide, was positioned at 45° above the substrate and 10 μl of silica bead suspension was pipetted between the substrate and blade. The substrate was then linearly translated at 500–550 $\mu\text{m}/\text{min}$ to deposit a monolayer of silica beads (Table S2). To promote a long-range order in the monolayer of Si nanoparticles, 100-nm polystyrene nanobeads was also mixed into the silica bead suspension at a final concentration of 4 vol% except for the 280-nm silica bead samples where polystyrene nanoparticles were not added due to an interference to silica hexagonal packing. After deposition on a whole glass slide of $3'' \times 1''$, the slide was cut and the deposition area was manually patterned into a 10 mm $\times$ 20 mm region for nanoimprinting. Beads outside the region were removed by a blade and wiped. This step is necessary to reach the desirable indentation pressure under the maximal available force on the universal testing instrument (Instron 5500 R). Subsequently, the slides were heated to 240 $^\circ\text{C}$ for 5 min to melt the polystyrene nanobeads, which strengthen the integrity of the silica monolayer and allow for multiple use of each deposition.

2.3. Nanoimprinting of aluminum thin films

An aluminum film of five micrometers thick was evaporated onto clean glass slides using an electron-beam evaporator (Indel Systems-2602). The e-beam gun was a Telemark 4 pocket gun assembly with the Telemark TT-6 power supply, and controlled with a Sycon Systems STC-200/SQ Deposition Rate Controller. The aluminium source was 99.99% pure. Glass slides were cleaned by piranha solution and evaporation was carried out at a starting vacuum level of 1.1×10^{-7} torr. The deposition rate was 2–5 angstrom per second.

The silica monolayer was then pressed onto the aluminum surface at a pressure of 30 kN/ cm^2 for 30 seconds using the Instron instrument to create a pattern of nanodimple arrays. This imprinting pressure was optimized to create dimples without cracking the glass substrates. As mentioned above, the silica nanoparticles were patterned onto an area of 10 mm $\times$ 20 mm to satisfy this pressure given the force specifications on the Instron instrument. The patterned aluminum was then ultrasonicated in ethanol for 10 minutes, rinsed with DI water, and dried by nitrogen gun before anodization.

2.4. Anodization of nanoimprinted aluminum substrates

Aluminum was anodized in phosphoric acid (Alfa Aesar, Cat# A18067) under vigorous stirring. The concentrations of phosphoric acid were varied from 0.6 M to 3 M for 280-nm samples, from 0.2 to 0.6 M for 410-nm samples, from 0.04 to 0.2 M for 500-nm samples, from 4 to 15 mM for 645-nm samples, and from 1 to 5 mM for 760-nm samples (Table S3). To prevent sample burning, the electrolyte stock solution was diluted to the desirable final concentrations using a mixture of DI water and ethanol at a volume ratio of 4:1. The electrolytic temperature was maintained at -7°C by situating in a Styrofoam box containing a mixture of isopropanol and tightly packed ice/dry ice. All samples were anodized for 1 hour using a DC power supply (Electronic Measurement Inc., TCR300T16). The anodization voltages (V_a) were initially chosen corresponding to the relationship of cell size (D_c in nm) = $V_a \times 2.5 \text{ nm/V}$ [28], i.e. 112 and 164, 195, 255, and 296 V to form AAO films with indentation periods of 280, 410, 500, 645, and 760 nm respectively. However, for indentation periods of 500, 645, and 760 nm, anodization current surged when the calculated V_a of 200, 258 and 304 V were applied. Instead, voltages were lowered slightly to 195, 255 and 296 V respectively to maintain an anodization current density in the low milli-ampere/ cm^2 range.

2.5. Sample Characterization

Nanofeatures obtained in this work were characterized using a field-emission scanning electron microscope (SEM – Hitachi 4300) and an atomic force microscope (AFM – Veeco di Dimension, D3100 V). The nanobeads, cell and pore sizes, and AAO film thickness were analyzed by ImageJ [29].

3. Results and discussion

The silica nanoparticles were synthesized in a range of 280 to 760 nm (Table S1). Using the convective deposition procedure developed by Gilchrist group [27], monolayers of silica nanoparticles deposited on glass substrates were obtained and are shown in Fig. 2(a1)–(a5). Within the monolayer, the nanobeads take a hexagonal close-packed arrangement over a long range. Moreover a large area of deposition on the order of square centimeters can be created in ~ 15 minutes (Fig. 1(b)). Such a process is scalable to accommodate flat substrates of any size and the mold is re-usable (Fig. S1). These deposited nanoparticles serve as imprinting molds to indent aluminum deposited glass substrates. After imprinting on aluminum substrate, homogeneous nanodimples are formed on entire imprinted area while narrow bands of silica nanobead occasionally came off from the mold edge (Fig. S2). The resulting nanodimples have a period matching the nanobead diameters (Fig. 2(b1)–(b5)). Indentation depths are calculated from the diameters of the nanodimple opening in SEM images by trigonometry. The averages of dimple depth are $73.45 \pm 5.08 \text{ nm}$, $68.80 \pm 5.56 \text{ nm}$, $56.78 \pm 3.52 \text{ nm}$, $42.97 \pm 6.42 \text{ nm}$, and $26.30 \pm 3.16 \text{ nm}$ for the 760-nm down to 280-nm samples, respectively. The depths of 760-nm and 500-nm samples are confirmed by AFM measurements (Fig. S3), which are $69.26 \pm 3.75 \text{ nm}$ and $53.53 \pm 5.23 \text{ nm}$ respectively, comparable to the calculated values.

Following the anodization process, the AAO porous structure forms a hexagonally packed cell array with the periods and arrangements consistent with those of the imprinting molds (Fig. 2(c1)–(c5)). In contrast to the few discrete cell sizes available using non-patterned flat substrate [13], this pre-patterning procedure allows tunable cell sizes through selection of imprinting molds of different particle diameters.

The regular ordered cell arrangement is not limited to the top surface, but maintained through the film thickness (Fig. 2(d1)–(d5)) as observed from the cross-sectional images.

The varying film thickness in Fig. 2(d) is a result of differences in electrolyte concentrations, which are discussed later in this paper. It should be noted here that although electrolyte concentration plays an important role in the film growth rate, it does not seem to impact the cell and pore geometry, which is different from pH-dependent cell arrangement in the self-ordering process [30].

Distinct from the self-organization process that takes hours of anodization to obtain hexagonally arranged pores, nanoindentation predefines the pore location and allows immediate formation of ordered pores [23, 24]. A comparison between anodization on patterned and un-patterned areas of the same sample is shown in Fig. 1(h). It is clearly observed that ordered pores form only in the pre-indented region. Thus, the patterning technique is effective in greatly reducing the reaction time and aluminum thickness to produce straight pores. This is especially beneficial for the anodization of deposited thin aluminum films.

When the cell sizes are inspected more carefully, it is found that the cell sizes range from 280 to 760 nm, matching the nanobead molds. The cell size increases linearly with the anodization voltage, governed through the relationship $D_c \approx V_a \times 2.6 \text{ nm/V}$ (Fig. 3). The proportionality is slightly off from previously reported value of 2.5 [28], due to the need to reduce voltage and avoid current surge when pre-patterned substrates with periods greater than 500 nm are used. The pore size (D_p) of 88 to 211 nm also increases linearly with the voltage and the relationship is $D_p \approx V_a \times 0.6 \text{ nm/volt}$. As the voltage increases, the porosity is found to vary between 6% and 9% approximately. This value is slightly lower than what has been reported for the self-ordering regime of 10% porosity, dictated by an optimal stress induced from the volume expansion. Disordered pores often do not follow the 10% porosity rule [30]. We demonstrate here that regular, ordered pores guided by pre-indented patterns also deviate from the 10% rule. This is likely a result of residual stress in the aluminum layer from the imprinting process. Since the pores can be widened in a post-anodization process, the lower-than-10% porosity after anodization should not limit AAO in practical applications where high porosity is desired.

Capability to continuously tune the cell size allows us to study the influence of electrolyte composition on the AAO formation at different voltages. To facilitate a comparison of electrolyte composition, we used phosphoric acid in all anodizations and varied only its concentration. While the cell and pore sizes are found to be independent of the acid concentration, the film growth rate varies greatly with acidity (Fig. 4). The overall film thicknesses were measured directly from SEM images and the average AAO growth rates were calculated. With all the patterned AAO films, the film growth rate increases exponentially with the acid concentration until a critical value is reached, at which the anodization current density surges within 60 seconds and the film growth becomes non-uniform or breaks down (Fig. S4). This critical concentration of phosphoric acid is found to rely on the anodization voltage. For anodization voltage of 164, 195, 255, and 296 V, the critical concentrations are 0.65, 0.24, 0.016, and 0.006 M, respectively (dash lines in Fig. 4). When anodizing a pre-patterned substrate with a period of 280 nm at 112 V, the reaction is stable for an hour even when the phosphoric acid concentration is 3 M. Thus, no critical concentration is identified in this case. The maximum growth rate is found to be around 1–2 $\mu\text{m/hr}$ in all cases, slightly lower than that reported of self-ordered mild anodization around 2–6 $\mu\text{m/hr}$ [20]. The overall lower growth rate is likely a result of low anodizing temperature [31] of -7°C used to maintain a current density in the low mA/cm^2 range.

The AAO growth involves movements of ionic species between electrolyte/oxide and oxide/metal interfaces under an electric field. The ion flux can be monitored by the current density in the anodization process (Fig. 5(a)). Inspecting the current density as a function of time, it

is observed that at the beginning of the anodization, there is a high current density, suggesting fast initial growth of AAO. The current density and growth rate then decrease over time until a steady state is reached due to the formation of AAO barrier at the bottom of the pores, which decreases the ion mobility. The steady state current density is found to be heavily dependent on the acid concentration under a fixed voltage. Taking 410 nm pre-indentation pattern anodized at 164V as an example, the steady state current densities are 6.1, 8.3 and 11.2 mA/cm² for H₃PO₄ concentrations of 0.2, 0.4, and 0.6 M, respectively. The corresponding average AAO film growth rates are 318, 556, and 792 nm (Fig. 5(b)). The dependence of anodization current on the acid concentration thus offers a means to control the AAO growth rate.

The anodization current is related to the electrolyte concentration, electric field, and temperature according to the following equation:

$$i = 2anv \exp\left(-\left(\frac{W - qaE}{kT}\right)\right) \quad (\text{Eq. 1})$$

where n is the ion concentration, ν is the jump frequency, a is the activation distance, W is the energy barrier and E is the interfacial electric field [32]. Although the applied voltage and temperature are critical parameters for an oxide formation, they are fixed for each AAO cell size. Thus, the only parameter that contributes significantly to the current density for a fixed cell size is the acid concentration. From a first inspection, it appears that the anodization current should scale linearly with the acid concentration. However, an increase of the acid concentration reduces the Debye length at the electrode surface and increases the local electrical field [33]. The exponential dependence of anodization current on the electrical field in Eq. 1 dictates the observed exponential relationship between the film growth rate and the acid concentration as seen in Fig. 4.

When anodization is compared among different indentation patterns or applied voltages, it is observed that the acid concentration decreases exponentially with the increase of the anodization voltage for a fixed growth rate (Fig. 6). This observation is consistent with Eq. 1: in the case that the current density (or growth rate) and temperature are constant, the ion concentration n is exponentially proportional to the electrical field, which linearly scales with the anodization voltage.

Although the AAO growth rate can be improved by increasing the acid concentration, it is still limited by a breakdown mechanism, where the current density surges rapidly and the oxide film grows non-uniformly (Fig. S4). Such breakdown is caused by an avalanche electron multiplication process by impact ionization [34]. Albella proposed a model that the breakdown voltage of anodic Ta₂O₅ film is dependent on the logarithm of electrolyte concentration. The relationship is a result of increased avalanche size with electrolyte concentration. Fig. 6 shows a similar dependence of electrolyte concentration and breakdown voltage for AAO formation and supports the model.

As the cell size scales with the voltage, fabricating a nanoporous AAO film with a cell size larger than 500 nm has been found challenging due to breakdown. Although multiple techniques have been investigated to suppress burning, such as the usage of a powerful heat sink and conditioning the electrolyte with alcohol or polyethylene glycol [20, 35, 36], only a few studies reported successful fabrication of nanoporous AAO with cell size above 500 nm. Ono *et al.* [37] obtained AAO with cell sizes in the range of 300 to 600 nm using various acids, but the size of the ordered domains were small, only extending a few microns. Chu *et al.* fabricated AAO cell sizes as large as 950 and 980 nm by anodizing in malic acid at 450 V and in citric acid at 370 V, respectively, but the pore arrangement was not well ordered

[38]. Fournier-Bidoz *et al.* [24] anodized pre-patterned aluminum in 0.3 M H₃PO₄ to control the cell size in the range of 150–500 nm, but claimed anodization above 200 V to be unstable. Jagminas *et al.* [39] varied the phosphoric concentration from 0.005 to 0.3 M and tested the breakdown voltage using aluminum of different acid purities and found a convergence point of a breakdown voltage at 260 V corresponding to a cell size of approximately 650 nm, which was suggested as the cell size limit for anodization in phosphoric acid. Distinct from the prior work, we demonstrate here long-range ordered nanoporous AAO with cell sizes as large as 760 nm is possible by anodization in phosphoric acid. This is achieved by the combination of nanoimprinting and careful consideration of the anodization condition, including the voltage, acid concentration and temperature. This largest cell size of 760 nm obtained here is not the physical limit of the process but determined by the maximum output voltage in our power source.

4. Conclusion

Imprinting an aluminum surface with silica nanobeads, along with carefully selecting anodization conditions such as voltages and concentrations of phosphoric acid, enables the fabrication of highly ordered nanoporous AAO film with a wide range of cell sizes using only a single step of anodization. In the procedure, the cell size is continuously tunable from 280 to 760 nm based on the imprinting molds and the anodization voltages. The film growth kinetics and reaction stability are controlled by the electrolyte concentration. More concentrated electrolyte solution yields a higher growth rate, although the acid concentration has to be kept below a critical level to avoid the breakdown phenomena. As the mold fabrication and imprinting process are easily controllable and scalable, large areas of AAO with a long range order and flexible cell size can be produced in a cost-effective fashion to enable the broader applications of AAO films.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Fig. 1.

Schematic showing the process to fabricate highly ordered nanoporous AAO thin films by nanobead imprinting. (a) The deposition of monolayer of tightly packed silica as the imprinting mold. (b) A continuous monolayer of nanobeads covering a 3" × 1" glass slide. (c) Imprinting of nanobead mold onto an aluminum substrate. (d) An SEM image of hexagonally packed nanobead array used in (c). (e) The resulting nanodimples on aluminum surface serving as pore nucleation sites in the anodization process. (f) An SEM image of the ordered array of nanodimples matching patterns on the imprinting mold. The inset is a high magnification image showing the arrangement of the indents. (g) An AAO film with a pore arrangement comparable to the imprint mold. (h) A comparison of cell arrangement between patterned and un-patterned areas on the same AAO film. Scale bars are 2 μm .

Fig. 2. SEM images showing the nanoparticle monolayers used as the imprinting molds (row (a)), the indented aluminum thin films (row (b)), surfaces of the anodized oxide films (row (c)) and cross-section views of anodized oxide films (row (d)). The features were created using monolayers of 280 nm (column 1), 410 nm (column 2), 500 nm (column 3), 645 nm (column 4) and 760 nm (column 5) silica nanoparticles, respectively. The images show a translation of the nanofeature arrangements from the molds to the AAO films. All scale bars are 2 μm .

Fig. 3. Relationship between the applied voltage (V_a , volt) and the resulting cell diameter (D_c , nm), pore diameters (D_p , nm), and porosity. The linear fit of the cell diameter versus voltage yields $D_c = 2.6038 \times V_a - 8.3497$. The pore diameter also increases linearly with the anodization voltage by $D_p = 0.5997 \times V_a + 21.91$. The porosity (P) was calculated as $P = (\pi/2\sqrt{3})(D_p/D_c)^2$, which varies between 6% and 9% in the cell size range fabricated.

Fig. 4.

Relationship between the electrolytic concentration and film growth rate for different nanoindentation periods. For all the cell sizes, the film growth rate (GR , nm/hr) increases with the acid concentration (C , mol dm⁻³). The best fittings for each series show an exponential growth rate: $GR = 311.3 \exp(0.3594 \cdot C)$ for inter pore distance of 280 nm; $GR = 219.34 \exp(2.187 \cdot C)$ for inter pore distance of 410 nm; $GR = 374.18 \exp(8.1051 \cdot C)$ for inter pore distance of 500 nm; $GR = 341.38 \exp(100.11 \cdot C)$ for inter pore distance of 645 nm; and $GR = 438.12 \exp(155.53 \cdot C)$ for inter pore distance of 760 nm. The dash lines indicate the critical concentrations leading to fast current surge within 60 seconds for each indentation period. Anodization of the 280 nm sample is stable even in the high concentration of phosphoric acid of 3 M.

Fig. 5. The profiles of current density of AAO film formed at 164 V in H₃PO₄ concentrations of 0.2M, 0.4M, and 0.6M (a) Current profile as a function of time for 60 min. (b) Current density and AAO growth rate as a function of the H₃PO₄ concentration.

Fig. 6. H_3PO_4 concentration as a function of the applied voltage for different growth rates. The black solid line predicts the critical concentrations which yield a breakdown.