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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

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 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

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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 500 nm, 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.

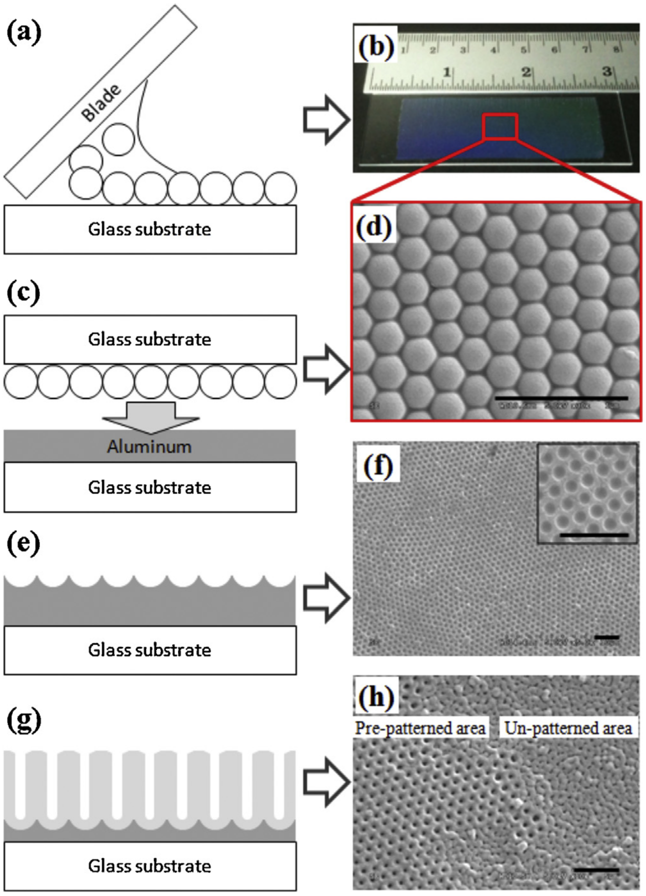

Fig. 1. Schematic showing the process to fabricate highly ordered nanoporous AAO thin films by nanobead imprinting. (a) The deposition of monolayer of tightly packed silica as the imprinting mold. (b) A continuous monolayer of nanobeads covering a 3" × 1" glass slide. (c) Imprinting of nanobead mold 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.

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 μm/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" × 1", the slide was cut and the deposition area was manually patterned into a 10 mm × 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 °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.