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Decoupling two-step anodization in anodic aluminum oxide

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It is well known that ordered anodic aluminum oxide (AAO) can be fabricated by a two-step anodization process, but in the current approach, pore size and interpore spacing are coupled because the ordering mechanism is expected to be the same in both steps. Here, we demonstrate that, by using a different approach during the second anodization step, we can vary the pore size independently (either shrunk or enlarged), while preserving the ordering of AAO inherited from the first step. This approach is based on changing the electrolyte in the second step, while applying the same voltage as the first step. These results imply that ordering in AAO is strongly dependent on the coupled effect of electrolyte and voltage in the first step, whereas ordering in the second step is only affected by the voltage, quite independent of the electrolyte used. With this decoupling, AAO template processing should become more versatile. © 2009 American Institute of Physics. [doi:10.1063/1.3257261]

I. INTRODUCTION

Anodic aluminum oxide (AAO), also known as porous alumina, is a self-ordered nanostructured material well-suited for use in electronic, magnetic, optical, and biological applications due to its small pore size (4–200 nm) and spacing (10–500 nm).^{1–9} Under slightly acidic conditions, both oxidation and dissolution of aluminum lead to the formation of pores. AAO pores form a self-assembled honey-comb structure with short range order over certain ranges of anodic potential and pH.^{10–12} Recently, it has been used as a template for synthesizing nanowires, nanotubules, nanorods, nanodots, etc., with high uniformity in the relevant dimensions. AAO is an attractive nanostructured material because it can be obtained reproducibly and economically.¹³

The achievement of highly ordered AAO films with the desired pore size and pore interval is the crucial step that dominates the feasibility of the successive fabrication and the properties of resultant nanostructures. Within the self-ordering processing windows,^{12,14–16} an ordered AAO fabricated by two-step anodization has a typical pore size and pore spacing which are dependent on the applied voltage.¹⁷ Fabrication of AAO beyond the processing windows with two-step anodization leads to a breakdown of ordering, even though the expected pore size and interpore spacing are maintained. In order to produce independent control of pore interval and diameter of AAO film, templated self-assembly (TSA) of AAO pores has been used.^{18,19} TSA can be achieved by pre patterning the substrate using interference lithography or imprinting, but it is expensive and cumbersome.

The limitation of the current processing windows is due to the conventional understanding that the two steps of a two-step anodization process should be coupled; namely, that it should be done with the same electrolyte and voltage in both steps. In this article, we demonstrate that this is not

necessary. Thus, with the decoupling of the two anodization steps, the pore size and interpore spacing of ordered AAO can be independently controlled.

II. EXPERIMENTAL

High purity Al foil (99.997% purity) was annealed at 500 °C for 3 h under N₂ atmosphere and was electropolished in a mixture of perchloric acid and ethanol [HClO₄(70%):C₂H₅OH=1:4 in volume ratio] at room temperature at 20 V for 20 s. The first step anodization was carried out in 0.3M H₂SO₄, 0.3M oxalic acid or 0.3M H₃PO₄, applying voltage of either 20 or 40 V for 3 h at 0 °C. The formed oxide layer was removed by a mixture of phosphoric acid (6 wt %) and chromic acid (1.8 wt %) at 60 °C for 1 day to ensure that the layer was completely removed. An ordered or disordered array of concave ditches remained on the Al surface, depending on the conditions of the first anodization step and these served as the sites to initiate the formation of a nanopore array in the second step of anodiza-

TABLE I. The summary of first and second step anodization conditions for samples 1(a)–1(j).

Figures	First step anodization condition		Second step anodization condition		Renamed
	Electrolyte	Voltage (V)	Electrolyte	Voltage (V)	
1(a)	H ₃ PO ₄	20	H ₃ PO ₄	20	P2P2
1(b)	H ₂ SO ₄	20	H ₃ PO ₄	20	S2P2
1(c)	H ₃ PO ₄	40	H ₃ PO ₄	40	P4P4
1(d)	Oxalic	40	H ₃ PO ₄	40	O4P4
1(e)	H ₃ PO ₄	40	Oxalic	40	P4O4
1(f)	H ₃ PO ₄	20	H ₂ SO ₄	20	P2S2
1(g)	H ₂ SO ₄	20	Oxalic	20	S2O2
1(h)	H ₂ SO ₄	20	Oxalic	40	S2O4
1(i)	Oxalic	40	Oxalic	40	O4O4
1(j)	Oxalic	40	0.01M H ₂ SO ₄	40	O4S'4

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FIG. 1. FESEM micrographs of fabricated AAO with different methods. (a) P2P2, (b) S2P2, (c) P4P4, (d) O4P4, (e) P4O4, (f) P2S2, (g) S2O2, (h) S2O4, (i) O4O4, and (j) O4S'4.

tion. The anodization condition for second step was carried out in different acids, at a similar or different voltage as the first step, also for 3 h at 0 °C. Characterization of the samples was conducted by field emission scanning electron microscopy (FESEM).

III. RESULTS AND DISCUSSION

The fabricated samples are summarized in Table I and renamed for simplicity. The anodization conditions for self-ordered AAO are well known, e.g., 19–25 V (Refs. 12 and 15) for H_2SO_4 , 40 V for oxalic¹⁴ and 160–195 V for H_3PO_4 .^{16,20} Anodizing beyond the ordering window pro-

duces disordered pore arrays. This is clearly shown in Figs. 1(a) and 1(c), where both the first and the second step are beyond the ordering window. For AAO formed by anodizing within an ordering window in the first step but outside the window in the second step, the nanopores are well-ordered [Figs. 1(b), 1(d), 1(g), and 1(j)]. However, for AAO formed by anodizing outside the ordering window in the first step but within the window in the second step, the nanopores are poorly ordered [Figs. 1(e) and 1(f)]. From these observations, we can conclude that the first step anodizing condition is the most crucial parameter to determine the ordering of the AAO film.

Figure 1(h) shows that when both steps of anodizing are carried out within different ordering windows, each using a different electrolyte and thus a different applied voltage, this results in poorly ordered nanopores. From here, one can notice that the most important parameter determining the ordering of the final AAO film is the applied voltage, i.e., the voltage in the second step must be same as that of the first step. This can be further confirmed by Figs. 1(b), 1(d), and 1(j), where a correct first step and an incorrect second step, which has the same voltage as the first step is able to produce well-ordered pores. Thus, we deduce that the ordering mechanism of two-step anodization is different from that of conventional single step AAO. The ordering in first step mainly depends on the combined effect of electrolyte and applied voltage, but applied voltage is the main contributor to the ordering in the second step.

To explain these phenomena, the TSA method, which induces periodic relief structures on the Al surface, can be considered to have the same effect as the concave structures formed on the Al surface after the first step. The indentation marks on Al surface (TSA) or the concave structures (after first step anodization) serve as the initial sites for pore formation in the first step. If the concave structure formed during the first step is ordered, the nanopore structures formed in the second step will also be ordered, if the applied voltage is the same as the first step. This is why AAO fabricated by conventional two-step anodization is always well-ordered.

The reason why the voltage in the second step must be the same as the voltage in the first step is because of the well-established interpore spacing rule of 2.5 nm/V. In order to fabricate an ordered nanopore array, the applied voltage in the second step must produce an interpore spacing that matches the spacing of the remnant structures of the first step—the concave structures—which necessarily mirror the interpore spacing of the first step. Thus, anodizing in a second step with a different voltage from the first step will produce a disordered array [Fig. 1(h)]. Hence, one can conclude that for ordering during the first step anodization a driving force is required, which is a certain volume change in Al during AAO formation leading to repulsive interaction between neighboring pores and ordering. Only the condition with moderate expansion of Al during AAO formation produces ordered structures. On the other hand, no ordered pore arrays can be fabricated in the case of contraction or very strong volume expansion.²¹ Once the ordering is accomplished, then only the suitable voltage (which controls the

interpore spacing) is needed to maintain the ordering. There is no requirement for another driving force to order the pores since they are already ordered.

With this phenomenon, different pore size of AAO can be fabricated, while preserving order. Figures 1(b) and 1(g) show the AAO pore size of 25 and 15 nm using H_3PO_4 and oxalic during the second step, respectively, while preserving the interpore spacing within the 2.5 nm/V rule, which is 50 nm, compared with the 10 nm which is fabricated by H_2SO_4 in both steps. By using oxalic acids in both steps, pore size with 30 nm can be fabricated [Fig. 1(i)]. The pore size can be shrunk or enlarged to 15 or 60 nm by using 0.01M H_2SO_4 [Fig. 1(j)] or H_3PO_4 [Fig. 1(d)] during the second step respectively. The interpore spacing for them is 100 nm which is within the 2.5 nm/V. The reason for using the 0.01M H_2SO_4 is to avoid overdissolution of oxide under high electric field which caused “burning” of the sample. From here, well-ordered AAO with either different pore size with same interpore spacing or different interpore spacing with same pore size can be fabricated by anodizing in different acids or mixture of acids.

IV. CONCLUSIONS

In the two-step anodization for fabricating ordered AAO, the first step is strongly affected by both electrolyte and applied voltage, while the second step is only affected by the voltage. Using this effect, the two steps can be decoupled, such that ordered AAO arrays with different pore size and interpore spacing can be fabricated as long as (i) the first step anodization condition is within a chosen ordering window and (ii) the applied voltage of the second step is the same as that of the first.

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