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A comparison between self-ordering of nanopores in aluminium oxide films achieved by two- and three-step anodic oxidation

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ABSTRACT

We report on the enhancement of naturally-occurred self-ordering of nanopores in anodic aluminium oxide (AAO) membrane by performing three step anodic oxidation. Two and three step anodic oxidation methods were used to achieve self ordering of nanopores and the ordering of nanopores obtained by the methods were compared. The current–time curves, recorded during anodization, elucidate an almost similar features for all three steps in both methods. Scanning electron micrographs (SEM) show hexagonally arranged nanopores in a way which forms highly ordered areas or ordered domains. Domains are placed beside each other like a polycrystalline structure after two and three step anodizing, while larger ones are clearly observed over the surface after three step anodizing. More uniform nanopores with narrower size distribution are observed for AAO films of three step anodic oxidation.

1. Introduction

The template synthesis is known as an elegant electrochemical approach for the fabrication of nanomaterials such as nanowires and can be considered as an alternative choice to the other sophisticated methods such as molecular beam epitaxy and nanolithography [1]. The fabrication method may include electrochemically synthesis of thin fibrils into cylindrical pores of the template [2].

Among the frequently used templates, anodic aluminium oxide films provide highly ordered pore arrangements due to the self-organizing process, introduced by Masuda et al. under the application of anodic oxidation process for two steps [3–6]. AAO membranes with pore density of 10^{10}–10^{12} cm^{-2}, are formed by anodizing Al in appropriate acidic electrolytes such as oxalic acid [4,5]. The typical structure of the film consists of a thin non-porous barrier oxide layer which lies adjacent to the Al substrate and a porous layer on the top [7–8]. The top layer contains an array of hexagonally close-packed cylindrical cells at the center of which a straight hole is located. The formation of the porous structure results from the effect of a dynamic mechanical equilibrium between the film growth at the aluminium-oxide interface and the field-assisted oxide dissolution at the oxide–electrolyte interface [6,7].

Most of the reports on obtaining highly ordered AAO have been focused on using two step anodizing process in which the duration of the first step has a considerable effect on the formation of highly ordered polycrystalline domains. As the duration of the first step increases, the domains in the bottom of porous oxide layer form on larger areas [3,7]. Therefore, the effect of the first step of anodization on the ordering of nanopores is remarkable to achieve better cell arrangements of nanopores. In this paper, we aim to demonstrate the effect of three step anodization of aluminium on the ordering of the nanopores in AAO films.

2. Experiments

High purity Al foil (99.999%) was used as substrate after cutting into 1×1.5 cm^2 sized rectangular samples. After annealing at 500 °C for 5 h, Al substrates were surface prepared under a sequence of chemical surface treatments in KOH 200 g/lit, Na_2CO_3 50 g/lit and HNO_3 50% (in vol.) solutions. Then, Al foils were eloctropolished in a mixture of $HClO_4$ and ethanol (1:4 in vol.) at 15 V_{dc} below 5 °C. Anodization was conducted under constant potential of 40 V_{dc} in 0.3 M oxalic acid electrolyte. The temperature of the electrolyte was maintained at 0 ± 2 °C during anodization using a cooling system. The solution was stirred vigorously in order to accelerate the dispersion of the heat that evolved from samples. For anodizing more than once, the oxide layer formed in the

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previous steps was removed by wet chemical dissolution in a mixture of 0.2 M chromic acid and 0.4 M phosphoric acid at 60 °C for an appropriate time depending on the anodizing time. Either the second or the third anodization steps were carried out under the same condition as the first step for different durations which will be described later. For each step, the variation of the anodizing current was recorded against time. In addition, ordered polycrystalline domains and the diameter of the nanopores were characterized using SEM on the top and cleaved surfaces of the AAOs. The histograms of pore diameter demonstrating the size distribution of produced pores were then derived based on SEM images. The domain areas were determined by first outlining the boundaries on SEM micrographs, counting the number of pores for several domains, converting these numbers to areas, and finally averaging.

3. Results and discussion

In order to investigate the effect of the third step anodic oxidation, series of samples were fabricated by two and three step anodic oxidation and their growth mechanisms and structures were studied. Figs. 1 and 2 show the current transients recorded for the two and the three step anodic oxidation processes. Figs. 1a and 2a illustrate the variation of anodizing current in potentiostatic mode at a constant voltage of 40 V for the first steps. As shown, there exists a region associated with almost uniform and constant values of current without any possible expected drop in the graphs. Any drop in current transients at the first stages of anodic oxidation process may occure due to the formation of an oxide layer. The observed smooth variation of current may be explained by

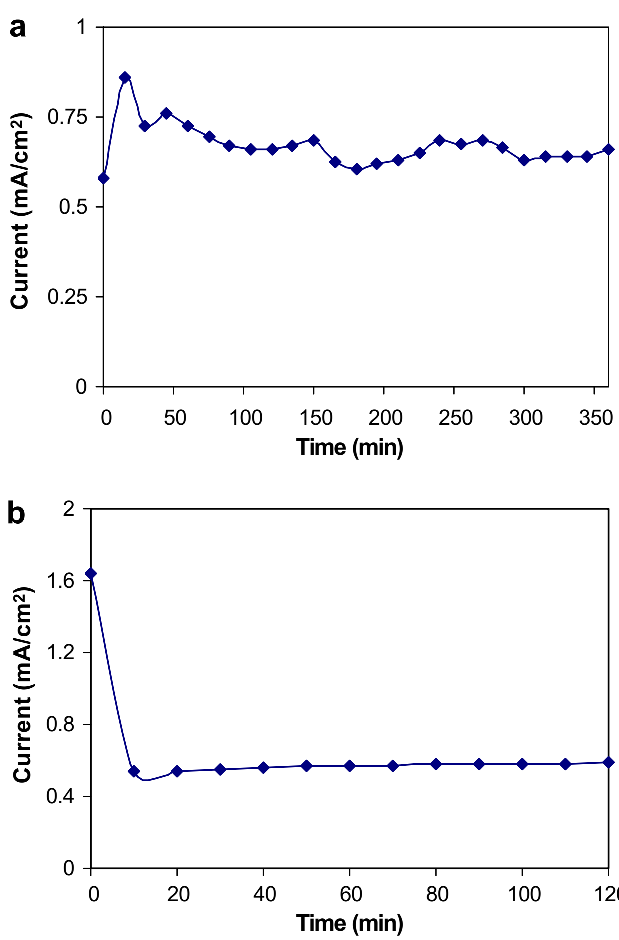

Fig. 1. Typical current transients recorded during the anodizing Al for two steps: (a) first step for 6 h and (b) second step for 2 h.

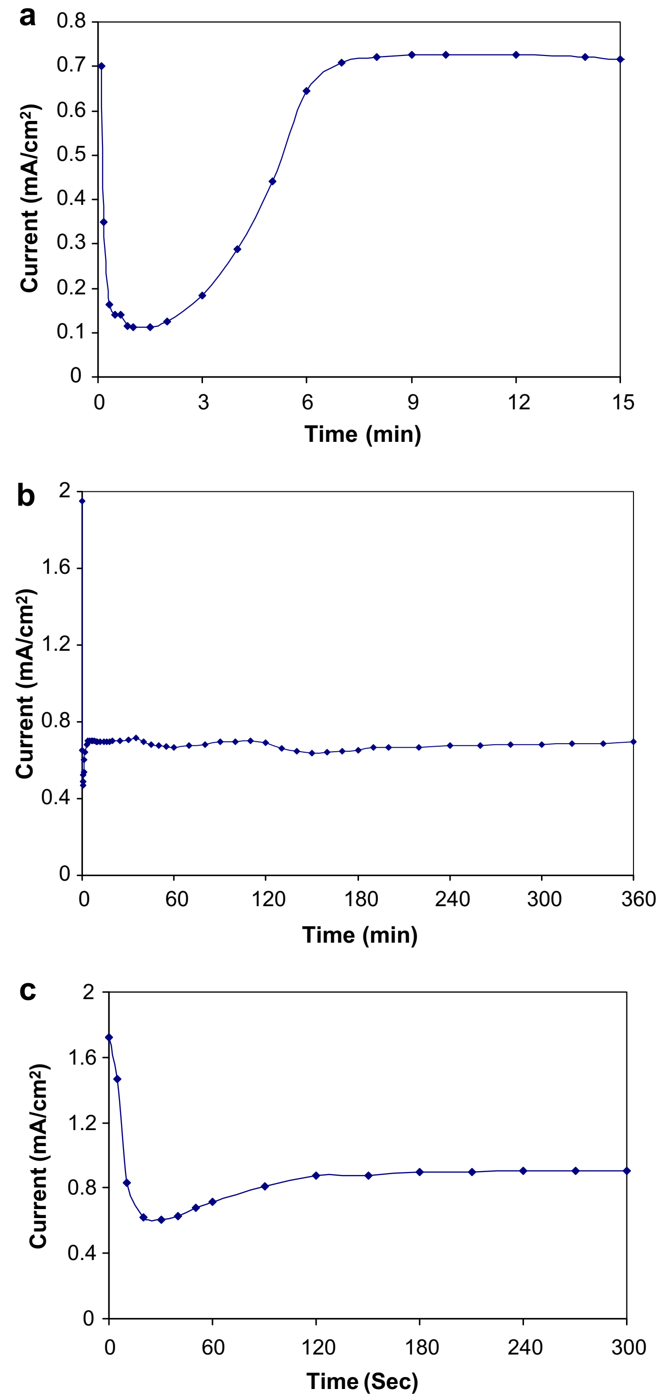

Fig. 2. Typical current transients recorded during the anodizing Al for three steps: (a) first step for 15 min, (b) second step for 6 h and (c) third step for 5 min.

the formation of an oxide layer on aluminium, naturally produced in the atmosphere on the samples during the rest time in the lab after electropolishing. The pre-formed oxide film may act as a barrier layer and further anodic oxidation develops the porous layer of AAO films. The current transient curves show plateaus regions in a range of 0.6–0.9 mA/cm^2 during first step which may be an evidence of the growth of porous film on the substrate. The current transients recorded for the second (Figs. 1b and 2b) and the third (Fig. 2c) steps just after dissolving the oxide layer show a drastic drop in the beginning of these steps. Since the second and the third steps were conducted immediately after dissolving the grown oxide layer at the first step, the sudden drop followed by a raise