



Structural engineering of nanoporous alumina by controlling the anodization voltage during the spontaneous current oscillation in hard anodization

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ABSTRACT

In aluminum anodization process the spontaneous current oscillation in certain electrolytes and anodization voltages can occur. The behavior of current in this process is called spontaneous oscillatory current otherwise we call the current behavior as non-oscillatory. The current difference between the spontaneous oscillatory and non-oscillatory conditions is appreciable (more than 50 mA/cm²) whereas to switch from spontaneous oscillatory to non-oscillatory behavior we only need to change the anodization voltage less than 3 V. The pore structure of porous anodic alumina film can be modulated by this oscillatory behavior. This effect occurs due to the variation of the anodization current which causes the variation of pore diameter along the pores. But by this procedure it is hard to control the structure of the pore as it is required, because the modulated structure mainly depends on the spontaneous current oscillation. In this article, it is shown that this spontaneous oscillatory behavior can be switched to nonoscillatory condition by changing the anodization voltage. Therefore by switching the anodization voltage between the spontaneous oscillatory and non-oscillatory behaviors, in any time interval, the pore structure of nanopore alumina can be engineered.

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1. Introduction

Ordered porous materials have been considered because of their potential application as photonic-crystal waveguides and other photonic devices, nanocomposites and biotechnology structures [1]. However, a serious challenge in the anodization process is the ability to fabricate ordered pore arrays with independently controlled spacing's and sizes. A number of new fabrication techniques that get close to the limits of conventional photolithography such as vapor-based deposition methods, copolymer block lithography, colloidal methods, sol-gel, template synthesis and self-assembly have been introduced [2–5]. Among them, the self-ordering process based on electrochemical anodization of materials such as aluminum, titanium, and silicon is one of the most popular non-lithographic approaches to design novel nanostructure materials and devices with new properties and functions [6].

Self-ordered porous anodic alumina (PAA) has been obtained by mild anodization (MA) within limited processing parameters such as voltage, electrolyte ... [7–10]. The accessible interpore distances and pore diameters are limited by the self-ordering regime. However, MA is slow (current density mainly is lower than 15 mA/cm² and oxide

growth rates about 2–6 μm h⁻¹ [12]) and requires several days of processing time to obtain PAA film that is suitable for applications.

Recently, a new method based on the hard anodization (HA) process was reported [11–14] for fast fabrication of highly self-ordered PAA with a wide range of pore sizes and interpore distances for practical applications. In this new method, in a controllable procedure, an excellent array of nanopores was obtained applying a high current density (400–800 mA/cm²) and oxide growth rates (50–100 μm h⁻¹) for a relatively short time (~1 h). High growth rate (25–30 times faster than MA) of anodization is a key factor in the use of this technique for various industrial applications.

Recently fabrication of ordered PAA films with periodically modulated diameters of nanopores has been introduced in several methods such as combining MA and HA processes, pulse and cyclic anodizations and pulse sprinkling of electrolyte [11,15–19]. In addition to these methods, some spontaneous oscillations of current during the HA process affect the pore structure. Lee et al. [20] observed the spontaneous current oscillation during the unstirred electrolyte (0.3 M oxalic) condition in high voltage (>130 V). This phenomenon could affect the pore structure during the current oscillation but it is hard to control the structure of the pore because the modulated structure depends on the spontaneous current oscillation.

As we know in hard anodization, it is possible to fabricate three dimensional PAA film by switching the anodization potential in fairly large intervals (more than 10 V) [15–18]. This switching can change

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the anodization current such that the variation of pore diameter takes places. But this kind of switching can effect on pore interval and ordering due to the linear relation between anodization voltage and interpore distance. Here we are interested to do the same process where only small change in anodization voltage is required. Therefore we use the spontaneous oscillatory behavior here, because the current difference between the oscillatory and non-oscillatory conditions is appreciable (more than 50 mA/cm^2) whereas to switch from spontaneous oscillatory to non-oscillatory behavior we only need to change the anodization voltage less than 3 V. In our previous work, spontaneous current oscillation was reported in HA condition in some specific voltage intervals in sulfuric oxalic acid mixture electrolyte [24]. Here it is shown, the anodization current is changed by switching the anodization voltage between the spontaneous oscillatory and non-oscillatory behaviors (due to different ranges of potential) thereby pore structure of PAA film was engineered.

2. Experimental

In our experiment a high purity aluminum foil (99.999% purity, 1 mm thickness) was used as a starting material. Prior to anodizing the aluminum foil was annealed at 400°C in air for 2 h and degreased in acetone. Then the samples were electropolished at room temperature in 25:100 volume mixture of HClO_4 and ethanol at constant current density at 25 mA/cm^2 for 3 min. The HA technique was applied using sulfuric/oxalic acid mixtures containing 0.4 M oxalic acid and xM sulfuric acid ($x = 0.07, 0.08$) as electrolyte. During the anodization the electrolyte temperature of all samples was kept constant at $0^\circ\text{C} \pm 0.1$. The electrolyte was circulated inside the anodization cell with high power pump to accelerate heat diffusion especially during a high current anodization. For all anodization process, a programmable power supply (EC1000S NF company) was employed. The preanodization step for 10 min was applied to produce a thin porous oxide layer (about 500 nm thick) to create a protective layer against burning at high voltages [11]. As we know in each electrolyte mixture [24] the appropriate voltage for pre-anodization is related to the current and we choose this voltage such that the current density to be in the range of $1.5 \text{ mA/cm}^2 < j < 2.5 \text{ mA/cm}^2$ [24]. After pre-anodization (in voltage lower than 35 V), the anodization voltage was increased to a final constant value by a suitable rate that is exactly related to the concentration of sulfuric acid [24]. To investigate the morphology and self ordering degree of nanopores, the SEM images were taken from the Al surface (imprint barrier layer) after selective etching of the porous alumina film by a mixture of 6 wt.% H_3PO_4 and 1.8% H_2CrO_4 at the end of each process. Beside the SEM images the Fast Fourier Transformation (FFT) of these images prepared to consider the pore ordering.

3. Result and discussion

As we know, mainly the anodization current during the potentiostatic HA of aluminum decreases almost exponentially as a function of time [12], unlike the case of conventional mild anodization where the current almost remains at steady state value during the anodization process [25]. As a result of fast growth of pore depth, such a current behavior for HA has been attributed to the diffusion-limited of ionic motion from pore mouth to pore bottom (barrier layer region) that leads to a decrease of electrochemical oxidation of aluminum at the pore bottom [12]. As far as we know in mild anodization no oscillations of current have been reported, but in potentiostatic HA Lee and co-worker reported the spontaneous current oscillation during the unstirred electrolyte condition [20]. As they showed current oscillation disappeared when stirring of the electrolyte was started and then appeared again when stirring was stopped. They suggested that the diffusion-controlled anodic oxidation of aluminum is responsible for this behavior. They have reported that during the current oscillation the anodic alumina exhibits

modulated pore structure, due to current profile. They have shown that it is hard to control the structure of the pores as it is required, because the modulated structure mainly depends on the spontaneous current oscillation. This type of current oscillation occurs only during the unstirred condition but recently we have reported that the spontaneous current oscillation during the potentiostatic HA of aluminum can be occurred [24]. This behavior is happening as the current decreases exponentially without stopping the stirring or changing the anodization voltage. Although here the purpose of this article is applying the spontaneous current oscillatory to fabricate three dimensional nanopores and not to study about the reason of the existence of this spontaneous current oscillatory behavior. We mention some reasons for this phenomenon. Based on our knowledge about the origin of the spontaneous current oscillatory behavior only a very few article have mentioned this effect in special case and condition. It seems that spontaneous current oscillatory here is a complicated phenomenon and may need many experimental and theoretical research to find out about this phenomenon but we think some physical and chemical parameters such as barrier layer temperature, diffusion path, chemical reaction at the interface, ionic motion inside the barrier layer, resistance and regional electric strength could respond for the existence of this phenomena. But the contribution of these parameters is not clear.

Self organization of nanoporous alumina can occur in sulfuric/oxalic acid mixture in different sulfuric concentrations and anodization voltages in MA [21,22] and HA [23] conditions.

As it was mentioned in previous work [24], in hard anodization the current behavior changes by increasing the anodization voltage for three different compositions of sulfuric/oxalic acid mixtures. Various anodization voltages and sulfuric concentrations in which the current density time curves exhibit exponential decay (ED), exponentially decay oscillation (EDO) and exponentially decay with an extra peak (EDE) are presented in Table 1. For example in 0.4 M oxalic, 0.08 M sulfuric acid mixture, as it is seen in Fig. 1(a), below the 46 V, current decays exponentially. But when the anodization voltages are in the range of 46 and 49 V, the anodization current behaves as an exponentially decay oscillation (EDO). In this case the cross section SEM micrograph, as a periodic structure, is shown in Fig. 1(b). Beyond this interval (for example $52.5 > 49$) the oscillatory behavior disappears and current shows the approximately exponentially decay with an extra peak (EDE). This behavior of current also for other mixture in different voltage has been observed [24].

In Fig. 2(a) four current peaks are shown and according to the SEM micrograph, Fig. 2(b), the current profile pattern is exactly transformed to PAA structure. Interval I in this figure is due to second current peak in current–time curve and interval II is corresponded to gap between current peaks 2 and 3. The length of interval I is proportional to the charge transferred during the second current peak and length of interval II is determined by the charge transferring between current peaks 2 and 3. As it is seen between the current peaks, the current density has lower magnitude therefore the charge transferring and pore growing rate are also slow. For this reason we can mention, length II < length I. As we know [17,19] for a structural engineering of PAA film it is required to transfer the charge between peaks controllably. It is worth to mention that the samples that are made in MA or HA exhibit different fracture modes along the vertical direction of PAA against external stresses. For MA PAA films, cracks

Table 1

Various anodization voltages and sulfuric concentrations in which the current density time curves exhibit exponential decay, exponentially decay oscillation and exponentially decay with an extra peak.

Sulfuric concentration (M)	Exponentially decay (V)	Exponentially decay oscillation (V)	Exponentially decay with an extra peak (V)
0.07	<53	53–56	56<
0.08	<46	46–49	49<
0.9	<43	43–46	46<

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