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Fabricating Al_2O_3-nanopores array by an ultrahigh voltage two-step anodization technique: Investigating the effect of voltage rate and Al foil thickness on geometry and ordering of the array

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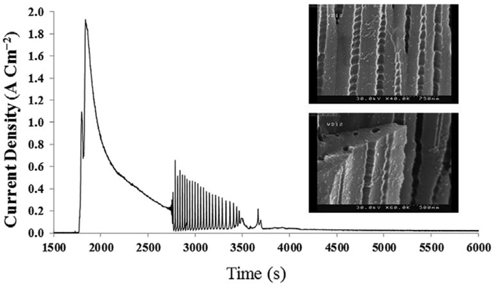
HIGHLIGHTS

- Fabrication of Alumina nanopores arrays by applying anodization voltage of 250 V.
- Investigating the effect of anodization voltage rate on nanopores arrays ordering.
- Investigating the effect of Al foil thickness on nanopores arrays ordering.
- Achieving 3-D periodic modulations of the aluminum oxide nanopores.
- Possibility to switch spontaneous oscillatory current behavior to non-oscillatory.

GRAPHICAL ABSTRACT



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ABSTRACT

A densely-packed hexagonal Al_2O_3 nanopores array was fabricated by using a relatively simple ultrahigh voltage two-step anodization method. The developed method was technologically simple and suitable for controlling the morphology and geometry of the nanopores array as a nanodevice which has specific applications in constructing biosensors. The anodization was carried out at different applied voltage rates and Al foil thicknesses. By increasing voltage, the current density showed a peak shape profile so that its maximum was directly depended on the rate of the applied voltage. The simulation curves evidenced direct dependency of the ordering of the nanopores to the anodization voltage rate. The most ordered array was achieved at an applied voltage rate of 0.600 Vs^{-1} when a 1.0-mm thick Al foil was used. Spontaneous oscillation patterns (self -oscillations) were appeared at the voltage rates of 0.300, 0.400 and 0.500 Vs^{-1} when a 0.25-mm thick Al foil was utilized. The cross-sectional SEM images revealed that a three-dimensional periodic modulation, along the interior surfaces of the nanopores has been developed.

1. Introduction

Fabrication of periodically-ordered nanomaterials such as nanopores, nanotubes and nanowires has resulted in widespread progress in nanotechnology toward nanodevice manufacturing.

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Now materials with exceptional mechanical, electronic, magnetic, catalytic and optical characteristics can be produced through decreasing their dimensions and accurate controlling of their surface geometry which is achievable by the combination of nanotechnology and surface engineering [1–3]. However, the developed fabrication methods must be effective and technologically simple. In this regard, bottom-up method has attracted much attention for fabricating self-organized nanostructured materials with periodical (highly ordered) arrangement of nanopores. For example, the self-organized process has been occurred during the anodization of aluminum in acidic electrolytes [4]. The method is a volume-expansion process, *i.e*, it is accompanied by a compressive stress along the interface of the metal and the oxide film which plays a significant role in self-ordering of oxide nanopores [5]. It should be mentioned that self-organization is a spontaneous process, *i.e.*, it is not necessarily directed or controlled by any agent or subsystem inside or outside of system [6]. However, improving the regularity and being able to place nanostructures, with preferred sizes, at desired locations are of the great concern [7].

Nanoporous anodic aluminum oxide (*AAO*) template is known as a versatile and inexpensive platform for constructing multitude nanostructures which exhibits intriguing device properties [4,8,9]. In its fabricating procedure, the surface of the aluminum substrate is first polished because the ordering of the self-organization pattern of the pores depends on the degree of the surface smoothness. To obtain a long-range pore order, the smooth surface is either exposed to multiple anodization-and-etching steps [10] or to a pre-patterning stage followed by a single-step anodization [11–14]. However, the latter results in a perfectly ordered nanopore lattice.

In hard anodization (*HA*), the current density is much higher than in mild anodization (*MA*) so that the rate of oxide growth increases up to about 3500-fold [15,16]. However, to avoid the breakage of the oxide film, the aluminum must be pre-anodized at a constant current density or at a constant potential for a period of few minutes. It should be noted that the high-electric field applied during *HA* promotes much evolution of heat, and any excessive heat should be effectively removed in order to prevent sample burning. However, for certain anodizing electrolytes, the temperature of electrolyte has been reported to have no influence on the self-ordering regime [15].

After discovery of the two-step anodization [10], the one-step self-organized anodization method has no longer been utilized due to production of low-ordered nanopores array. The two-step anodizing procedure is frequently used for constructing the highly-ordered nanopore arrays on an aluminum surface in acidic solutions such as sulfuric, oxalic, or phosphoric acid as the electrolytes.

In this work, for the first time, the effect of voltage rate increasing has been involved in the two-step anodization process of aluminum as a parameter that could affect the order of nanopores array. The morphology of the resulting *AAO* nanopores, under the effect of voltage rate increasing and Al foil thickness, have been characterized and discussed. So far, to the best of our knowledge, voltage rate increasing and substrate thickness have not been considered as effective parameters in two-step anodization process.

2. Experimental

Phosphoric acid, oxalic acid, perchloric acid, ethanol and acetone were supplied from Merck chemical company. Aluminum foil was supplied from Sigma-Aldrich chemical company. Double distilled water was utilized in all experiments.

All electrochemical experiments were carried out using a GW Instek power supply model GPR-30H100, an MDK power supply, and a GWINSTEK dual display multimeter model GDM-8255A connected to a personal computer to investigate the voltammograms and the bulk electrolysis process. A FUNGILAB sonicator, a LAUDA ECOLINE chiller model RE 206, and two MEGATEK pumps (models MP-3005 and MP-6003) were applied in order to avoid overheating. The morphologies of the obtained films were examined using a Hitachi S-4160 scanning electron microscope.

The high-purity (99.999%) aluminum foils with thicknesses of 0.25 and 1.0 mm were punched to make discs with diameters of 12 mm. Each disc was degreased in acetone and ethanol and then washed with deionized water. To have a disc with a smooth surface, an electropolishing system was designed (Supporting Information). The disc was used as the working electrode (anode) while an aluminum plate was utilized as the counter electrode (cathode). For electropolishing, a constant potential of 20 V was applied for 300 s at zero degree of centigrade (Supporting Information). The electrolyte solution was 1:4 (v/v) perchloric acid in 99% ethanol.

For anodization purpose, the aluminum disc was used as anode in a set up similar to the electropolishing system as mentioned above. In this set up, the anode was cooled by using two MEGATEK pumps as their roles were described in our already published article [17]. Briefly, the electrolyte solution was sprinkled toward the aluminum sample in order to control the heat transfer and avoid sample burning. Initially, the anodization step was carried out under a mild anodization process by applying a voltage of 40 V for 600 s while a mixture of oxalic and phosphoric acids, with a concentration of 0.3 M with respect to each acid, was used as the electrolyte solution. The anodization voltage was linearly increased up to 250 V and was kept constant at this potential level for 8000 s (hard anodization).

3. Results and discussion

3.1. Effect of voltage rate on anodization of aluminum

In HA process, voltage was increased by various rates and kept constant at 250 V for an anodization period of 8000 s. The ratio of the interpore distance (in nm) to the anodization potential (V) is reported to be considered about 2 in HA processes [17]. Therefore, a potential of 250 V was applied to fabricate pores array with interpore distances (cell diameter) of 500 nm as this array has been reported to provide high sensitivity in extraordinary optical transmission (*EOT*) measurements [18]. It should be noted that the anodization period improves the order of nanopore arrays in works where electrolyte solutions such as sulfuric, oxalic, phosphoric [19], and malonic acids [20] were used. Furthermore, the anodization period rearranges the cells and reduces the number of defects and dislocations in the nanopore structure [4]. Anodization voltage rates of 0.045, 0.055, 0.065, 0.075, 0.085, 0.100, 0.150, 0.200, 0.300, 0.400 and 0.500 Vs^{-1} were applied when a series of Al discs with a fixed thickness of 0.25 mm was used as substrates. For the Al discs with a fixed thickness of 1.0 mm, the voltage rates were of 0.500, 0.600, and 0.700 Vs^{-1}. It should be noted that applying higher voltage rates, depending on thickness of the disc, would result in samples burning which is technically not possible to be avoided by cooling the system through sprinkling of the electrolyte as discussed before. In fact, a local temperature distribution is developed over the anode surface which causes a non-uniform current flow. This consequently affects the thickness uniformity of the fabricated anodic film as well as the thickness of the barrier layer. This means that the formation of thicker oxide at the central area of *AAO* could be the result of a local current associated with the local temperature rise. This causes development of distorted pore channels at the lower part of *AAO* [5]. For the Al discs with thicknesses of 0.25 and