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Self-ordered porous alumina membranes with large lattice constant fabricated by hard anodization

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Abstract

We report on the fabrication of self-ordered porous alumina with long interpore distance. The samples were prepared in an oxalic acid solution using hard anodization process. In contrast to the common two-step anodization process, this technique only consists of a single step, where a much higher voltage is applied. The as-produced samples were examined and analysed in detail by scanning electron microscopy. The results show that the porous structures produced by hard anodization have larger interpore distance of 310 nm as compared with the conventional two-step anodization, where this distance can vary between 90 nm and 120 nm. Moreover, the porous-layer growth rate is about 10 times faster. Then the qualitative analysis of Fast Fourier transform was applied on high-resolution SEM surface images. The results confirm a good hexagonal pore ordering. The pore diameter distribution revealed the fact that pores have uniform size of 170 nm with standard deviation of 7 nm.

Keywords: Porous alumina; Hard anodization; Fast Fourier transformation; Self-ordering

1. Introduction

In the last decades the scientists have been focused on nanostructured porous materials because of their unique geometrical properties. Such nanoporous materials are very suitable as a template for synthesis of functional nanostructures [1–7] or they can be also used for fabrication of various nanodevices, e.g. solar cells [8,9], photonic crystals [10–13] or magnetic storage [14].

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Among others, the ordered porous alumina (OPA) plays an important role in nanotechnology because of its easily tuneable morphological properties, relatively low-cost production and wide range of applications. The porous alumina has been investigated over the last 50 years [15], but the breakthrough became in 1995, when Masuda and Fukuda have produced for the first time the self-ordered porous alumina membrane using the so-called two-step anodization process [16]. Thereafter, the scientific interest in the OPA has significantly increased. In summary, the OPA nanostructures with nanopores hexagonally arranged into close-packed domains must be fabricated under specific conditions known as "self-ordering regimes" [16–22]. This means that the OPA morphology such as the pore diameter and the interpore distance strongly depend on the anodizing parameters and especially on the acid solution and anodizing voltage [18]. The interpore distance–voltage relation show a linear dependence in the ranges of 19–25 V for sulphuric acid [17,18], 40–60 V for oxalic acid [16,18,21] and 160–195 V for phosphoric acid [18,19,22]. The correspondent interpore distances for these voltage ranges are 50–60 nm, 90–110 nm and 400–500 nm, respectively. If the anodizing parameters are set outside of the optimum range, it leads to the extreme decrease of the ordering degree for the resultant structure. The gap between 100 nm and 400 nm in the interpore distance of OPA gives drawback from the viewpoint of possible applications. Recently, Lee et al. have discovered a novel approach to fabricate OPA with large interpore distance between 220–300 nm [23]. In principle, this fabrication process combines the so-called hard anodization [24,25] (that was widely used in industry since 1960s) and the specific conditions from standard two step anodization. This important finding has significantly contributed to the expansion of applications based on the ordered porous alumina.

From the application viewpoint it is necessary to determine the quantitative and qualitative properties of ordered porous alumina with large lattice constant produced by the hard anodization technique. Therefore, this paper is focused on the study of ordering degree and pore uniformity of OPA structures using high-resolution images from scanning electron microscopy (SEM) and the image post-processing using Fast Fourier transformation (FFT) [26].

2. Experimental

The samples were prepared from high purity (99.999%) aluminium (Al) foils (Godfellow Cambridge Ltd.) with 0.25 mm thickness. The preliminary aluminium treatments were firstly annealing in an inert ambient at 400 °C for 2 h and then the foils were electropolished in ethanol and perchloric acid solution (4:1) to obtain smooth-surfaced samples for anodizing. The anodization was performed in 0.3 M oxalic acid solution cooled to 1 °C. The system was connected to a potenciostatic control that has the following profile: first, the standard anodization (SA) is set to 40 V for 5 min. (Fig. 1, region A), then the voltage increases quickly from 40 V to 140 V at a rate of 0.8 V/s (Fig. 1, region B), and finally the high voltage is maintained constant at 140 V for 1 h to perform the so-called hard anodization (Fig. 1, region C). In order to control hard anodization the applied voltage must be set below the upper limit of 150 V, otherwise the current density rises above a critical value and the sample is burnt. The anodized sample was then washed in deionized water and ethanol. The remaining aluminium substrate was immersed in mixture of 0.1 M copper dichloride and 20 wt% hydrochloric acid ($CuCl_2 + HCl$) until the freestanding OPA membrane was achieved. In order to open the pore bottoms, the OPA membrane was etched in 5 wt% phosphoric acid for 20 min.

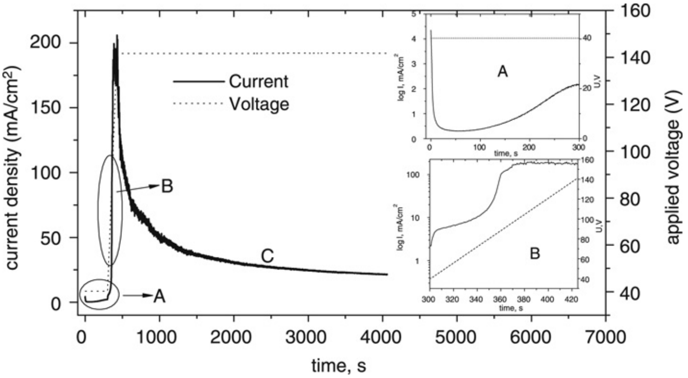

Fig. 1. The current density and applied voltage versus time characteristics. The solid line corresponds to the current density and dashed line to the applied voltage profile. The current characteristics consists of three regions: A, where the pre-anodizing step with 40 V is shown (see in inset A), region B belongs to the time dependence during the voltage ramp from 40 V up to 140 V with rate of 0.8 V/s (see inset B), and finally region C shows the time dependence for the hard anodization of 140 V for 1 h.

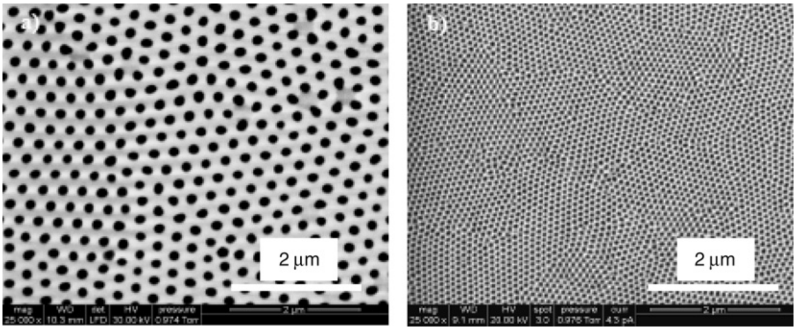

Fig. 2. The SEM surface images of ordered porous alumina produced in 0.3 oxalic acid: (a) hard anodization at 140 V and (b) conventional 2 step anodization at 40 V.

3. Results

The as-produced OPA membranes were examined by scanning electron microscopy (SEM–FEI Quanta 600). The SEM images of different OPA membranes are compared in Fig. 2: (a) the bottom surface of a sample produced in 0.3 M oxalic acid and 140 V, (b) the top surface image of OPA anodized in standard two step process using 0.3 M oxalic acid and 40 V. In comparison, the porous structure from HA (Fig. 2(a)) has the larger distance between pores around 300 nm and also a bigger domain size between 2–3 µm compared to SA samples (Fig. 2(b)). Similarly as in the SA samples, we can observe that each pore is hexagonally enclosed by six neighbouring pores. This confirms very high ordering degree of HA porous structure. According to cross-section SEM analysis in the Fig. 3, the thickness of 88 µm was measured after one hour of hard anodizing process and the pore growth rate is 10 times faster than in the case of standard anodizing. The inset in Fig. 3 reveals that the pores are regularly straight from the top to bottom.

Fast Fourier transform (FFT) analysis was carried out for SEM high-resolution images of OPA samples produced by HA [26]. FFT of the SEM image representing the pore pattern over

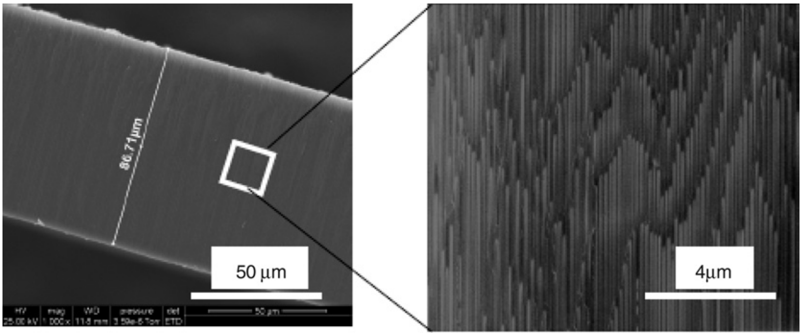

Fig. 3. On the right is the SEM image from cross-section view of OPA performed in hard anodization. The thickness of 87 µm was measured. On the left, there is magnified zone from the cross-section.

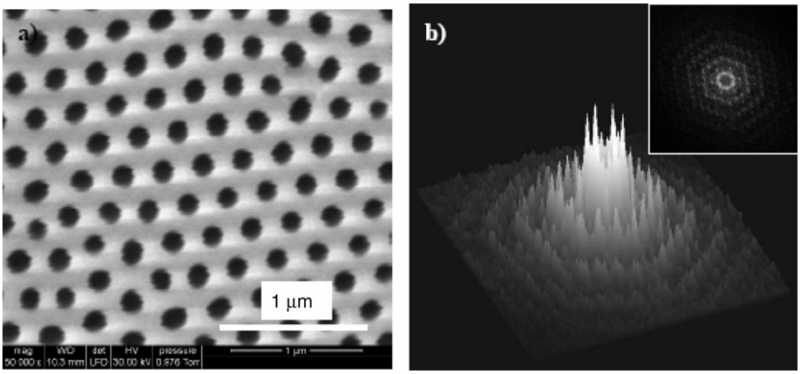

Fig. 4. (a) The high-resolution SEM surface image with area of 8 μm^2 and (b) 3D Fast Fourier transformation (FFT), where the inset represents the original FFT domain.

the sample surface provides the information about the geometrical periodicity in the reciprocal space. In theory, the ideal model for a pore array with a perfectly ordered triangular lattice has a FFT pattern consisting of a reciprocal hexagonal array. The Fig. 4(a) represents the SEM surface image of OPA with area of 8 μm^2. In order to perform the FFT analysis, the source image was first threshold to obtain a binary image. Fig. 3 shows the FFT power spectrum in logarithmic scale of the studied image. The FFT domain consists of various hexagons revealing the fact that the source image is highly ordered. Moreover, the Fig. 4(b) illustrates six very high and narrow peaks arranged into the circle. This confirms quite perfect sixfold ordering of pores over the surface, while the ring shape predicts some periodicity imperfection in the ideal hexagon.

The pore diameter distribution of OPA produced by HA was studied using particle analysis [26]. A simplified SEM surface image of OPA with an area of 30 μm^2 and with 369 pores was analysed. The pore diameter distribution is illustrated in Fig. 5. A Gaussian curve was fitted to the distribution. The centre of Gaussian curve from Fig. 5 gives a mean pore size of 169 nm and a standard deviation of 7 nm. This confirms quite narrow pore size distribution over a large surface area. The porosity of as-produced samples was estimated to be approximately 28% (total area of 369 pores divided by studied area of 30 μm^2). The pore density was calculated to be approximately 1.23×10^9 pores per cm^2.

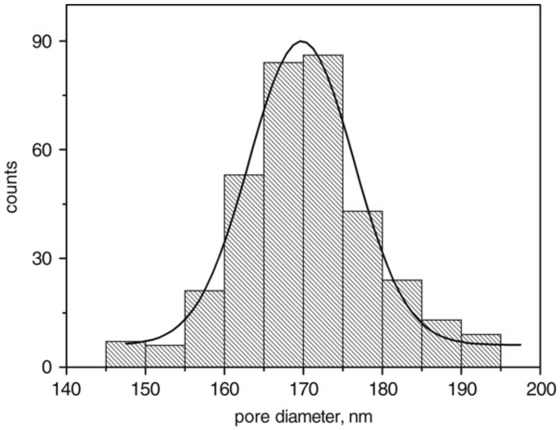

Fig. 5. The pore diameter distribution analysed from 369 particles (pores) found on the OPA surface with area of approximately 30 μm^2. The curve represents the Gaussian fit histogram data with the centre at 169 nm and standard deviation of 7 nm.

4. Conclusions

Ordered porous alumina membranes were successfully produced using a novel fabrication process called hard anodization. This process has several advantages compared with the conventional two step anodization: (i) the self-ordered porous alumina produced in hard anodization is feasible only in a single fabrication step, (ii) the HA process is more effective because the oxide growth rate is almost 10 times higher (80 μm/h) than in the case of standard anodization and (iii) we can achieve a newly discovered large lattice constant of 300 nm for the resultant porous alumina structure. FFT analysis of the SEM images from the as-produced membranes showed out a high ordering degree of hexagonally arranged pores over the surface. The particle analysis of the SEM images confirms a very good uniformity in the pore size. The interpore distance, the high pore ordering and the particular optical properties of such porous alumina, make these structures very promising candidates for realizing photonic bandgap materials for visible wavelength.

Acknowledgements

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