

Initial stage of pore formation process in anodic aluminum oxide template

N. Wang¹, W. Zhang², J. Xu¹, B. Ma¹, Z. Zhang¹,
Q. Jin^{1,*}, E. Bunte², J. Hüpkes², H. P. Bochem³

¹*Laboratory of Advanced Materials, and Department of Optical Science and Engineering, Fudan University, Shanghai 200433, China*

²*Institut für Energieforschung 5, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany*

³*Institut für bio und nanosysteme, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany*

Abstract

The initial stage of pore formation and the growth process in anodic aluminum oxide (AAO) template have been carefully investigated. Detailed features are found concerning the nanostructure configuration formed on the electropolished aluminum foil and the additional fine structures in the first and second anodization resulting from the current limitation effect during the beginning time of about 2 seconds. It would be helpful to make clear the mechanism of the pore-organizing process of AAO template.

* Email: qyjin@fudan.edu.cn

1. Introduction

Porous anodic aluminum oxide (AAO) films have received increasing interest because of their potential applications in data storage, sensing, optoelectronics and photonics, etc. [1-4]. Researchers have successfully improved the fabrication technique of AAO template [5-7]. Highly ordered self-organizing structures are achievable in a broader regime and novel three-dimensional porous architectures are realized by pulse anodization of aluminum. Besides, people also have been concentrating on the study of AAO growth mechanism. Several models have been proposed to explain the self-organized porous structure within AAO. It is generally accepted that mechanical stress resulting from the volume expansion during oxidation promotes the formation of ordered hexagonal pore arrays. The growth of porous alumina contributes to the equilibrium of oxide growth at the metal-oxide interface and field-enhanced dissolution at the oxide-electrolyte interface [8-9]. Theoretical understanding of the initial stages of pore growth indicates that pore formation is initiated by the activation energies of the interfacial reaction and the elastic stress caused by the volume expansion [10-11]. Nonetheless, we still lack enough experimental proofs for these models. Especially, details at the very beginning of the pore formation remain unclear.

In this work, we report the existence of nanostructure patterns with shallow vertical depth on the surface of electropolished aluminum foil, which can not be easily explained by former models based on both field distribution and mechanical stress. The dependence of the topography properties on the anodization time has been investigated to gain more insights into the incipient pore-organizing process of the AAO template. In addition, the effect of the limited current signal on the initial pore structure is investigated, which comes from the overflowed power supply (setting at the constant-voltage mode) in the first few seconds of anodization process. This is expected to help us understand the formation mechanism of AAO template and better control the fabrication technique.

2. Experimental details

The experiments were carried out in a self-made glass cell. A platinum mesh worked as a cathode and the aluminum foil as an anode. The distance between the cathode and anode was maintained at 4.1 cm and the area of aluminum foil exposed to the electrolyte was $0.81 \pi \text{ cm}^2$.

High purity aluminum foils (99.99%) were pre-annealed at 500 °C for 5 h under forming gases (95%N₂+5%H₂) to obtain homogeneous conditions for pore growth over large areas. The foil was etched in 2 M NaOH aqueous solution until bubbles occurred over the surface and then ultrasonically cleaned with de-ionized water. After degreasing by ethanol, it was electropolished in a mixture of HClO₄ and C₂H₅OH (1:10 by volume) under a constant voltage to lower the roughness of the aluminum surface. Anodization was carried out in 0.3 M aqueous oxalic acid at 5 °C for varying lengths of time ranging from 1 to 600 s [9]. In order to study the influence of the periodic concave pattern on the pore-organizing process, a standard two-step method was adopted. The first anodization was conducted at 40 V for 1 h and the formed

alumina was stripped away by immersing the foil in a mixture solution of H_3PO_4 (6wt%) and H_2CrO_4 (1.8wt%) at 60 °C for 30 min.

All voltages and currents were produced and recorded by a PC-controlled SourceMeter 2400 (KEITHLEY instruments, Int.) system. The responded current-time curves were used to monitor the anodization process as well as to analyze the growth mechanism. Field-emission scanning electron microscopy (FE-SEM) measurements were performed by a Leo Gemini FE-SEM working at 20 kV.

3. Results and discussion

Aluminum foils with the mirror-like surface are obtained after being electropolished under 20 V for 15 min. The morphology of this smooth exterior is detected by FE-SEM with high resolution and shown in Figure 1 ((a) 50K times, (b) 400K times magnification). From the top view of the electropolished film (see Fig.1(a)), where the brightness of spots reflects fluctuation on the surface, we find nanopattern structure existing on the whole aluminum foil. Some pinholes are also observed on the surface, which could be points where dislocations emerge. Enlarged scale in Fig. 1(b) lets us see clearly that there is an arranged porous structure on the surface with disordered quasi-circular pore shapes and a large size distribution. The typical interpore distance (D_{int}) is about 55 nm. Irregular holes are thought to be a fusion product of two or three circular holes. Some controllable nanostructures with relatively straight channels and small D_{int} have been achieved via improving the pre-treatment of electropolishing. A more detailed analysis of its influence on the structural properties of AAO template will be reported elsewhere. Former models can not easily explain why porous configuration exists after polishing treatment during which no alumina film formed. Aborative experiments are designed to study the pore-organizing process.

The anode current as a function of the anodization time is plotted in Figs. 2(a) and 2(b) for the first and second anodization, respectively. Typically for both cases, the current starts with a high value, decreases quickly to a nadir, and then increases to the stable value. The time when the current reaches its lowest point is about 43 s and 24 s, and that for current becoming a constant value after anodizing is around 10 min and 150 s, respectively. This indicated that pore-organizing process is much faster under the guiding of the concave pattern. Besides the above normal behavior for current evolution curves, we find that the recorded current maintains at the value of 105.5 mA during the first two seconds though we set the power in a constant-voltage mode at 40 V. This is because that the SourceMeter 2400 has a full-scale reading of 105.5 mA for the current measurement at 200V V-Source range. The power supply actually provides a limited current signal of 105.5 mA rather than a constant voltage at 40 V in the initial two seconds. By setting the electric source as a constant current supply at 105.5 mA, we obtain that the feedback voltage has a linear relation with time until 5.5 s from 0 to 95 V, as shown in Fig. 2(c). Thus, the aluminum foil is actually anodized at a linearly increased potential (constant current) for 2.3 s and then at a fixed voltage of 40 V. The working state of SourceMeter 2400 is also confirmed

on its panel display.

In order to study the pore-organizing process, especially the initial pore formation within 2.3 s before the voltage reaches 40 V and its effect on the succeeding process, we fabricate a series of samples with varying length of anodization time ranging from 1 s to 10 min, which covers main formation stages of the AAO template. Figs. 3(a) to 3(e) show the surface topography of aluminum foils anodizing at 40 V for various time in the first anodization. White spots are observed on the surface of samples anodized for 1 s and 5 s (Fig. 3(a) and (b)), which probably originate from the anodization in a fixed current mode at the beginning. This is confirmed by the surface of the sample anodized at a small voltage of 5 V for 5 s (no power limitation when the 20 V V-Source range is selected), where white spots are much clearly observed, as shown in Fig. 3(f). As we know from the linear dependence of D_{int} on the anodization voltage [12], D_{int} of AAO template anodizing at 40 V should be about 110 nm. But we obtain a nanopattern structure with much smaller value of D_{int} (typically around 50-60 nm). This attributes to the anodization under small voltages coming from power limitation and the guiding of electropolished surface. Comparing Fig. 3 with Fig. 1, we find that the pore-organizing process starts immediately after switching on the bias and tends to form the structure based on the nanopattern remaining on the surface of the electropolished aluminum foil. After several seconds (larger than 2.3 seconds), final voltage of 40 V is reached. The constant current anodization process is replaced by the constant voltage one. White spots almost disappear, and D_{int} is found to increase through a way that some pores stop growing as the anodization time goes on (as indicated by circles in Figs. 3(d) and 3(e)). The pore formation process enters an equilibrium stage after anodizing for about 10 min (deduced from the curve of Fig. 2(a), morphology shown in Fig. 3(e)).

After removal of the alumina layer, the patterned aluminum foil is used for the second anodization. Figs. 4(a) and 4(b) display the morphology of the patterned substrate viewed from the top and at an angle of 60 degree. Ordered hexagonal structure with concave patterns and D_{int} of about 110 nm are observed on the surface. This self-organized periodic structure serves as a mask for the following second anodization.

Fig. 5(a) shows the exterior topography of AAO template anodized at 40 V for 30 seconds in the second anodization. Same as what we have mentioned in the first anodization, the second anodization within the initial several seconds performs a fixed current process before the setting voltage of 40 V is reached. Previous studies have proved that the hexagonal structures are developed even under ultra-low anodic potentials [13]. Pore-organizing process is an immediate action after switching on the bias. It is reasonable that the oxidation at the current-limited signal leads to instability which develops into nanopattern structures with smaller D_{int} under the effect of field-enhanced dissolution. This introduces a mismatch between this nanopattern structures and the previous self-organized concave masks. Then, what we would expect at the beginning of the second anodization is the formation of small shallow patterns along the electric field direction superimposing on the hexagonal concaved template [14], as schematically depicted in Fig. 5(b). The SEM image in Fig. 5(a)

presents this superimposition result that some steps exist in the inner of pores (indicated by arrows).

Figure 5. (a) Top-view FE-SEM micrographs of AAO membranes anodized for 30 s in the second anodization; (b) A schematic diagram of the initial pore-organizing process of AAO under the guidance of the concave pattern structure.

Figure 6. Top view FE-SEM micrographs of AAO membranes anodizing at 40V for 10s to 600s in the second anodization

Morphology changes over the processing time in the second anodization are disclosed in Figure 6. All the images are recorded under the same magnification condition so that the size of topography can be directly compared. White spots are clearly observed on the surface of samples anodized for 10 s and 25 s, and then gradually vanished under the field-enhanced dissolution. This observation is consistent with the trace study of AAO template that the initially formed oxide locates on the film surface [15]. No step-inside-pore feature exhibits on the surface of sample anodized for 10 s, which attributes to the fact that the growth process plays a dominant role at this stage. With the increasing effect of dissolution, the fine step structure appears and becomes very distinct. Although the recorded current maintains at a constant value after anodizing for 150 s (shown in Fig. 2(b)), changes of the surface morphology continue. Concave masks, as well as steps inside pores, gradually disappear after 10-minute anodization, which signifies the accomplishment of pore-organizing process.

4. Conclusions

The pore-organizing process of AAO template, especially at the beginning stage of anodization, is detailedly discussed. Pore formation begins immediately after switching on the anodic bias, and is incipiently guided by the nano-patterned fluctuation originated from the electropolishing treatment of the aluminum foil. An unexpected current-limited signal from power limitation within the first 2.3 seconds is discovered to master the initial stage of anodization. The morphology of nanopatterns with a smaller D_{int} in the first anodization and the additional fine step structure in the second anodization are observed. The feature that the AAO template growth is much sensitive to the disturbance of small anodizing potential makes the above results possibly useful in fabrication of ordered AAO templates with ultrahigh density for some small devices.

Acknowledgments

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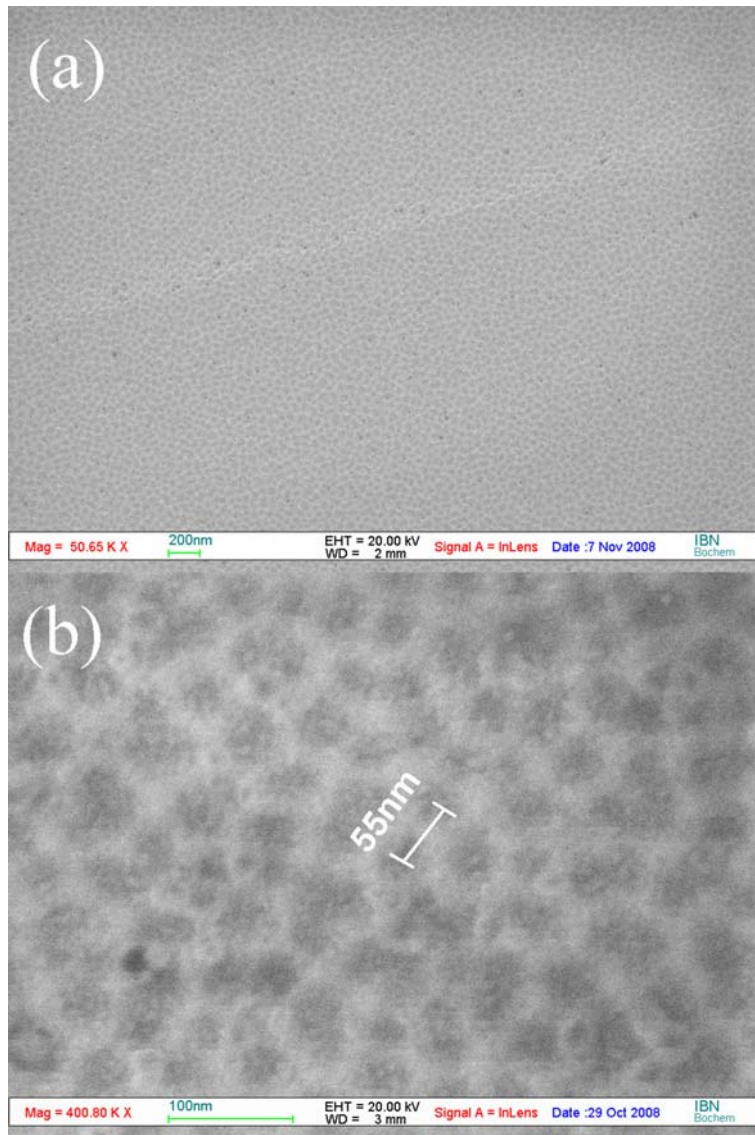


Figure 1 (a) 50K \times and (b) 400K \times times enlarged FE-SEM images of the aluminum surface electropolished at 20 V for 15 minutes.

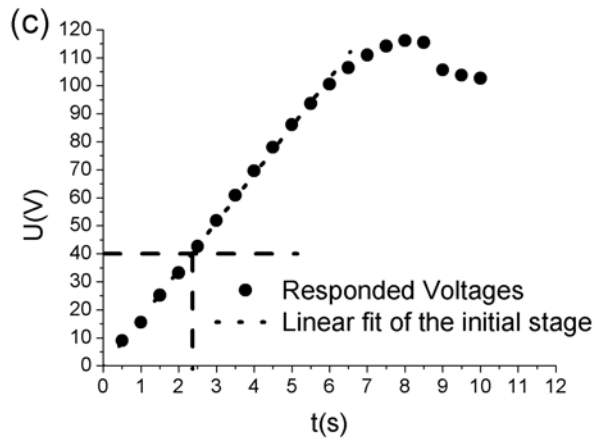
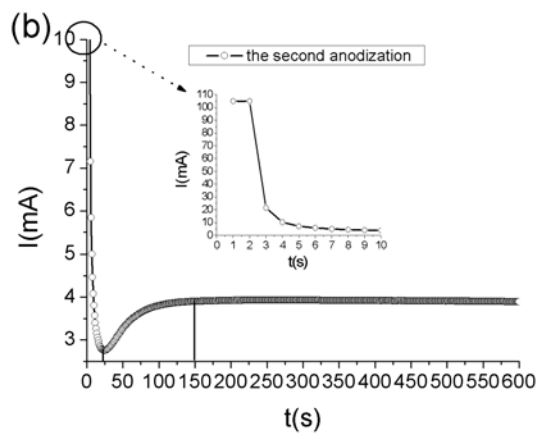
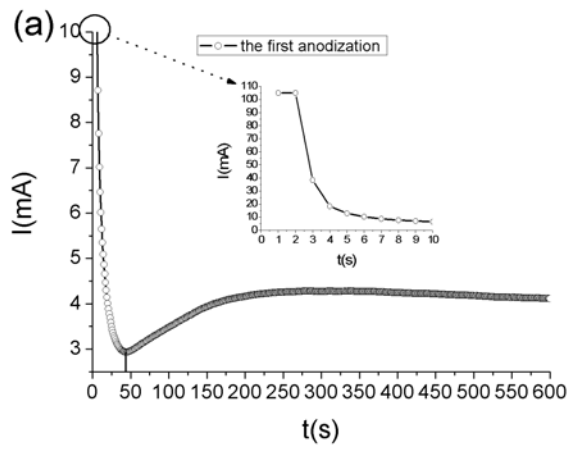


Figure 2. The anode current as a function of time in the (a) first and (b) second anodization, (c) the responded voltage and the linear fitting setting the power as a constant current supply at 105.5 mA

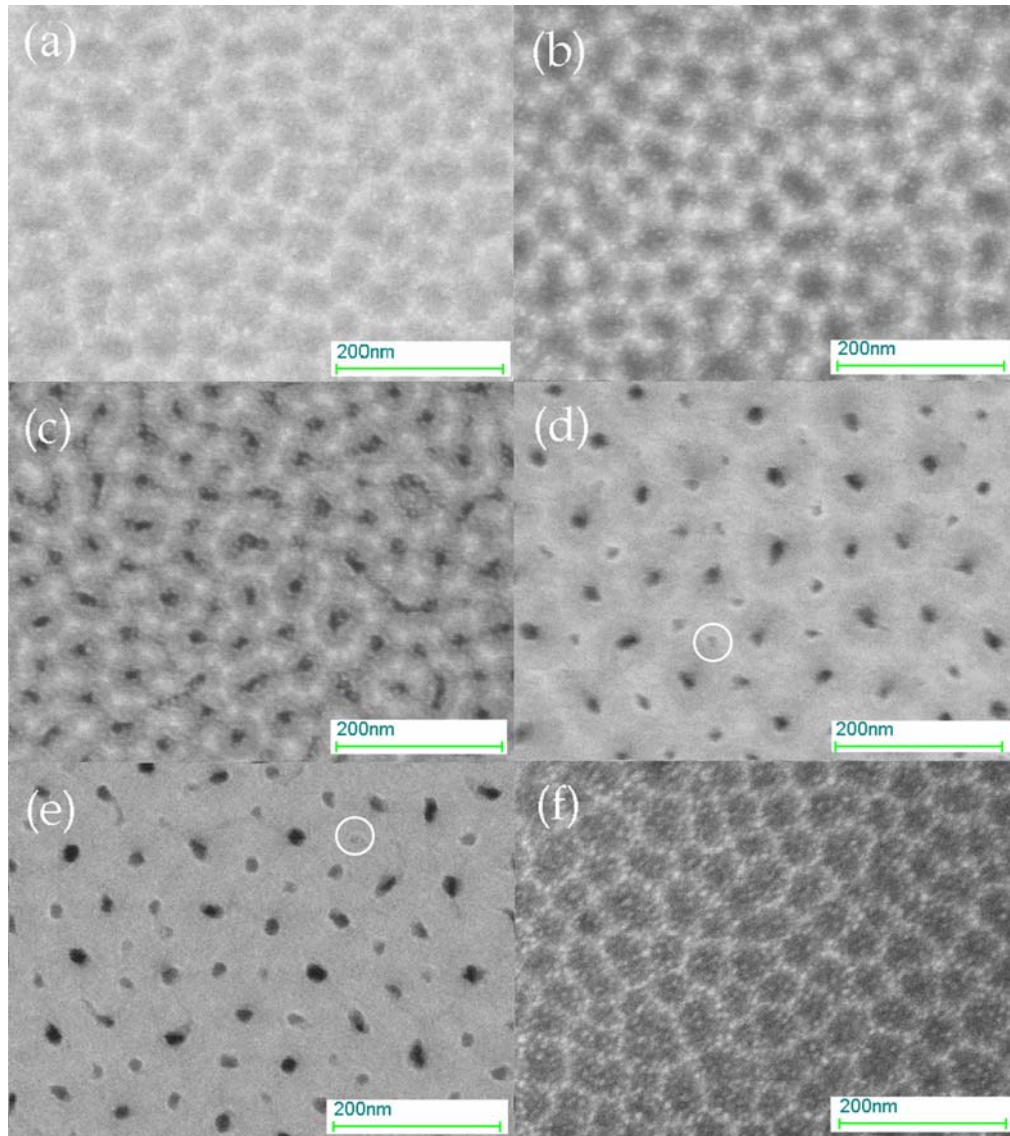


Figure 3. The FE-SEM image of AAO films formed in the first anodization, which are obtained under anodizing potential of 40 V for 1 s (a), 5 s (b), 40 s (c), 300 s (d), 600 s (e), and of 5 V for 5 s (f) on the electropolished aluminum surface.

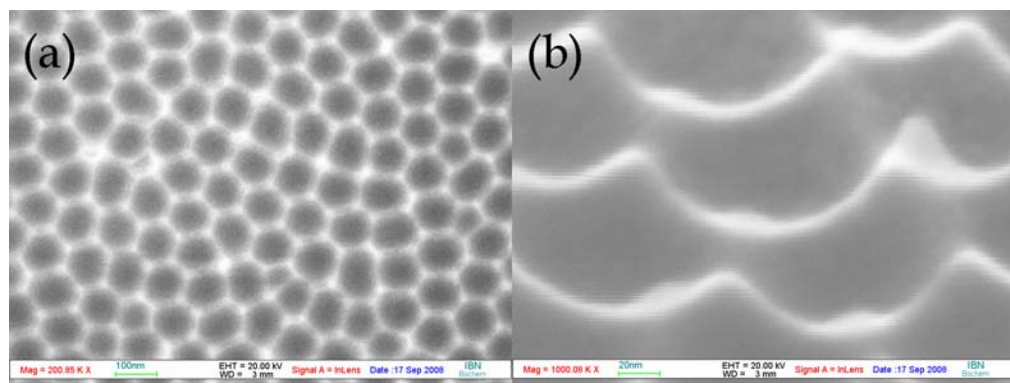


Figure 4. FE-SEM images of the aluminum substrate used for the second anodization, which are observed at an angle of (a) 90-degree and (b) 60-degree.

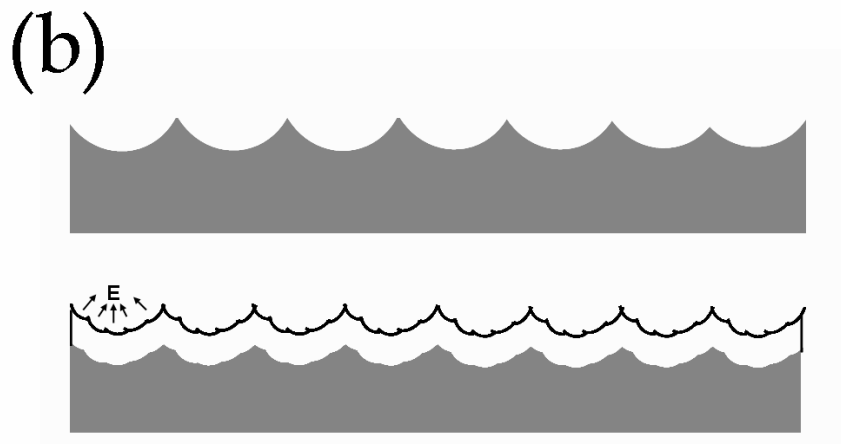
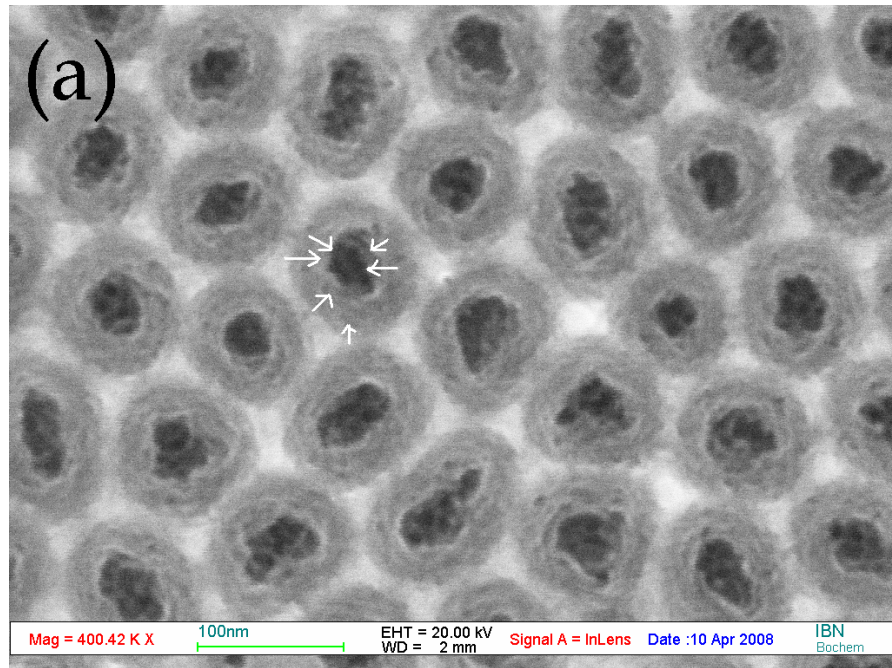


Figure5. (a) The top-view FE-SEM image of the AAO film anodized for 30 s in the second anodization; (b) A schematic diagram of the initial pore-organizing process under the guiding of concave patterns.

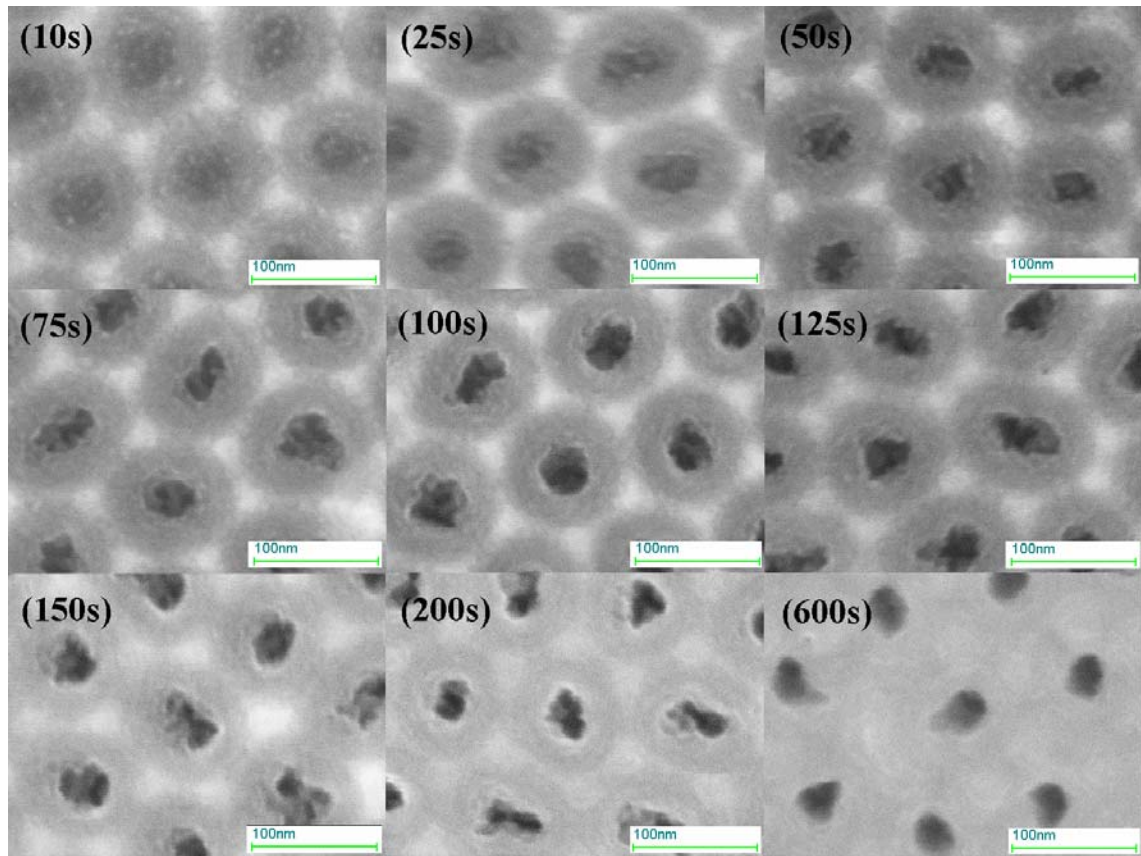


Figure6. The FE-SEM image of AAO films anodizing at 40V for 10 s to 600 s in the second anodization