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Formation of layered structure porous type anodic alumina films locally with a solution flow type micro-droplet cell

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**Abstract**

A solution flow-type micro droplet cell with co-axial dual capillary tubes (Sf-MDC) was applied to form porous type anodic alumina film with layered structure at selected areas on aluminium. The anodizing process with different repetition numbers, yielding different oxide layer numbers was performed with the Sf-MDC. The investigation of cross sections of the formed oxide showed that the pore diameter widened at the boundary between layers. From a simulated anodizing process with the Sf-MDC, the reason for this modification of the pores was suggested to be intermittent anodizing with processes of drying up of the solution of the pores and widening at the bottom of the pores.

Keywords: solution flow type micro-droplet cell, porous type alumina, anodizing, layered structure, pore widening

## Introduction

Anodic aluminum oxide films with an ordered nano-structure, porous type anodic alumina films, have attracted much attention<sup>[1-15]</sup>. The size and length of the pores are controlled by the anodizing conditions, including the concentration and temperature of electrolytes, and voltage. Thompson reviewed the barrier and porous type anodic alumina film formation on aluminum developed by anodic polarization in specific electrolytes<sup>[2]</sup>. Chu et al. reported on the fabrication of various ordered nano-porous alumina films with arbitrary pore intervals from 130 to 980 nm by a critical-potential anodizing approach with sulfuric, phosphoric, oxalic, glycolic, tartaric, malic, and citric acid electrolytes at 70 - 450 V<sup>[6]</sup>. Song et al. investigated the anodizing behaviors of aluminum in concentrated oxalic acid solutions and at high temperatures<sup>[10]</sup>. Zheng et al. reported that the formation of hydrophobic oxide films on aluminum by anodizing in phosphoric acid solution followed by desiccation and that a high contact angle surface formed on aluminum samples showed superior corrosion resistance. Vázquez et al. reported on the gas sensing properties of nanostructured anodized Zr-W oxide films using porous type anodic alumina layers<sup>[17]</sup>.

There are reports on the formation of localized anodic oxide films and a number of techniques for the formation of anodic oxide films on metal surfaces, locally, including coating, lithography, and laser methods have been proposed. Kamp et al. reported that the formation of porous type alumina at local areas using masks for back-contact back-junction solar cells<sup>[18]</sup>. However, these techniques present disadvantages in the complex processes involved. One technique that gets around these problems is the droplet cell technique<sup>[19-22]</sup>. One of the authors reported the application of a solution flow-type micro droplet cell with co-axial dual capillary tubes (Sf-MDC) to form porous type anodic alumina film locally. The thickness of the oxide film increases with decreasing speed of movement of the cell, and the growth rate of the oxide film was greatly affected by the specimen temperature<sup>[19, 20]</sup>. The same researcher also reported the formation of an oxide film with layered structure<sup>[21]</sup>, however, the fine structure between the layers and its formation mechanism have not been clarified. The purpose of this study is to clarify the fine structure between the layers of formed porous type anodic alumina films, and also determine the formation mechanism of the layered structure in the formed films.

## **Experimental**

### **Specimen and electrolyte**

Here, 99.99 mass% Al sheets (20 x 30 mm, 300  $\mu\text{m}$  in thickness) were used for the specimens. The specimens were cleaned in each of ethanol and highly purified water in an ultrasonic bath for 600 s. Then, the specimens were electropolished in  $13.6 \text{ kmol m}^{-3}$   $\text{CH}_3\text{COOH}$  (Kanto Chemical Co. Ltd., 99.7 mass%) /  $2.56 \text{ kmol m}^{-3}$   $\text{HClO}_4$  (Kanto Chemical Co. Ltd., 60 mass%) at a constant voltage of 28 V for 150 s at 278 K. After the polishing process specimens were cleaned with highly purified water and acetone. The solution used as the electrolyte for the anodizing was  $0.22 \text{ kmol m}^{-3}$   $\text{C}_2\text{H}_2\text{O}_4$  (Kanto Chemical Co. Ltd., 99.5 mass%) solution.

### **Anodizing with Sf-MDC**

The Sf-MDC and the experimental setup used in this study is the same as that reported previously<sup>[19-21]</sup>. An electropolished specimen was set on a computer controlled pulse-XYZ stage, and the specimen temperature during the anodizing was controlled by a Peltier device at 323 K. The cell was filled with electrolyte via a solution pump, then a droplet of electrolyte was formed at the tip of the inner capillary by adjusting the solution flow rate to  $8.1 \times 10^{-10} \text{ m}^3 \text{ s}^{-1}$  and a vacuum pressure of 80 kPa at the vacuum pump. After the droplet of electrolyte was formed, the distance between the inner capillary tip and specimen was adjusted to about 20  $\mu\text{m}$ . Thereafter, the droplet was put in contact with the specimen surface, and a constant voltage of 50 V was applied. The moving speed of the specimen was controlled at  $2.0 \mu\text{ms}^{-1}$  and distance was 4 mm for the formation of the oxide film lines.

### **Anodizing with macro-cell**

To determine details of the mechanism of the pore structures formed by anodizing with the Sf-MDC, a simulated anodizing process with the Sf-MDC was carried out with a traditional macro-cell. For the anodizing with the macro-cell, specimens were sealed to an exposed size of 10 x 10 mm, using the same electrolyte and applied voltage as in anodizing with the Sf-MDC. A Pt plate was used as the counter electrode, and the electrolyte was stirred. The procedure for the simulated anodizing by the macro-cell was as follows: 1) anodizing for 332 s at 298K or 323K, then 2) removing the specimen from the electrolyte and drying for 0 s or 1648 s at 298K or 323K in the air. From the

variations in the anodizing and drying conditions, six different conditions were examined. To simulate the repetition of anodizing with the Sf-MDC, the procedures 1) and 2) were repeated 5 times.

### **Observation**

Specimen surfaces after anodizing were examined by an optical microscope (WAYMAER Inc., BM-3400T) and scanning electron microscope (SEM, JEOL Ltd., JSM-6510LA) equipped with an energy dispersive X-ray spectroscope (EDS). The cross sections of the formed oxide films were observed by SEM. The specimens for the cross sectional observation were prepared by simple curving and breaking. Before the SEM observations, a thin Au layer was sputtered (Fin coater, JEOL Ltd., JFC-1200) on the specimens.

### **Results and discussion**

#### **Formation of porous type anodic alumina with Sf-MDC**

Figure 1 shows an example of change in current during the shuttling back and forth for the anodizing with the Sf-MDC with the repetition number as the abscissa. Fluctuations are observed in the current, however, the average of the current at each repetition (average current) shows very similar values of about 50  $\mu\text{A}$ . The average current is related to the growth rate and width of the formed film line. This result indicates that there is no change in the growth rate and width of the formed film line with up to 5 repetitions. The fluctuations observed in the current may be induced by the moving (motion) of the specimens, because the pulse XYZ stage was used for the formation of the film lines. The observed current during the anodizing shuttling back and forth with the Sf-MDC at each experiment showed some variation because the droplet size and distance between the inner capillary tip and specimen were not well controlled.

To investigate the effect of the repetition number of the anodizing with the shuttling back and forth on the growth rate of the film, the average current at each repetition was plotted with its repetition number, and Figure 2 shows an example of this plot. At a repetition number lower than 20 there is no significant change in the average current, from around 20 repetitions it decreases to about half, however, and again shows almost constant values. This result suggests that the growth rate of the film line decreases at a repetition number above 20.

Figure 3 shows optical microscope surface (left column) and SEM (right column) images after anodizing at different repetition numbers. There are lighter line parts (4mm in length) in the optical microscope images. From the EDS analysis of cross sections of the areas of the films, these have Al and O peaks. Independent of repetition number, nano-sized ordered pores are observed. These results suggest that this technique makes it possible to form porous type anodic alumina on the specimens locally, however, the width of the formed oxide lines show some variation.

Figure 4 shows cross sectional SEM images of a broken off part of the formed oxide film, (a) the film overall, (b) area magnified for further investigation, and (c) magnified area with a boundary. The counted number of layers conforms with the repetition number of the shuttling back and forth. It can also be seen that there is a widening of the pores at the boundaries between layers. Further, the (a) and (b) images show that the adhesiveness between the layers is low, and a separation of single layers has occurred. This result may be useful to achieve a novel formation technique for porous alumina layers with open pores. If applied in the field of membrane filter manufacturing, this may offer the potential of manufacturing accurately defined membrane structures.

### **Formation of porous type anodic alumina with a macro-cell**

To investigate the reasons for the pore widening at the boundary between layers, a simulated Sf-MDC anodizing process was performed with a traditional macro-cell. The solution temperature during the anodizing, and the duration of the drying process between the anodizing steps and the anodizing temperature was varied.

Figure 5 shows surface SEM images of anodized specimens with different anodizing temperatures and drying conditions. Except for specimens anodized at 298K and without drying, nano-sized pores are clearly observed, and larger sized pores are observed at the higher anodizing temperature at similar drying conditions.

Figure 6 shows cross sectional SEM images of broken off parts of oxide films formed at different anodizing temperatures and drying conditions. Independent of the anodizing and drying conditions, nano-porous structures are observed. The layer structure is only observed with specimens anodized and dried at 353K. This result suggests that repetition of anodizing and drying at the high temperature is important for the formation of the layered structure oxide films.

Figure 7 is a schematic representation of the formation process of the porous type alumina film with layered structure and widening of the pores at the boundary between layers. During the 1st scan (passage for anodizing) of the droplet, porous type alumina film is growing under the droplet, and the droplet then moves on leading to drying up of the solution in the pores and condensation of the electrolyte at the bottom of the pore. Next passage makes contact with the droplet at this position, pores are again filled with electrolyte and creating an extreme environment of high concentration electrolyte and high temperature at the pore bottom. This leads to pore widening at the pore bottom, and then the film resumes growth. Again the droplet leaves the position, and drying up occurs again. The repeated wet and dry cycles at the high temperature is the reason for the formation of these porous type alumina films with layered structure and with widening of the pores at the boundary between layers.

## Conclusions

A solution flow-type micro droplet cell with co-axial dual capillary tubes (Sf-MDC) was applied to form layered structure porous type anodic alumina on aluminum at a selected area. The formed porous type alumina film has a layered structure with widening of the pores at the boundary between the layers. From the simulated anodizing condition with a macro-cell, periodic anodizing with drying up and at high temperatures are the reason for the formation of the unique layered structure porous type anodic alumina films.

## Acknowledgments

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### **Caption list**

Fig. 1 Example of changes in the current during the anodizing shuttling back and forth with the Sf-MDC.

Fig. 2 Changes the in average current at each anodizing repetition plotted with the repetition number

Fig. 3 Surface optical microscope (left column) and SEM (right column) images after anodizing at different numbers of repetitions.

Fig. 4 Cross sectional SEM images of broken off parts of formed oxide films, (a) overall view of the film, (b) magnification of area for investigation, and (c) magnified image of a boundary layer.

Fig. 5 Surface SEM images of anodized specimens anodized at different anodizing temperatures and drying conditions.

Fig. 6 Cross sectional SEM images of broken off parts of oxide films formed with different anodizing temperatures and drying conditions.

Fig. 7 Schematic representation of the formation process of the porous type alumina film which has a layered structured with widening of the pores at the boundary between layers.

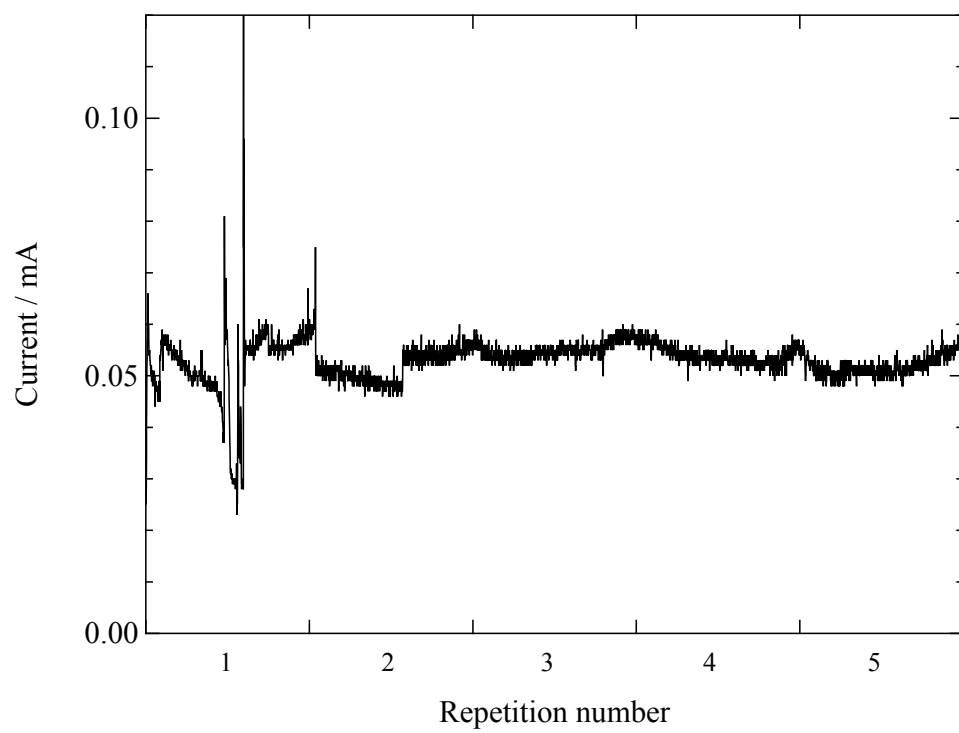


Fig. 1

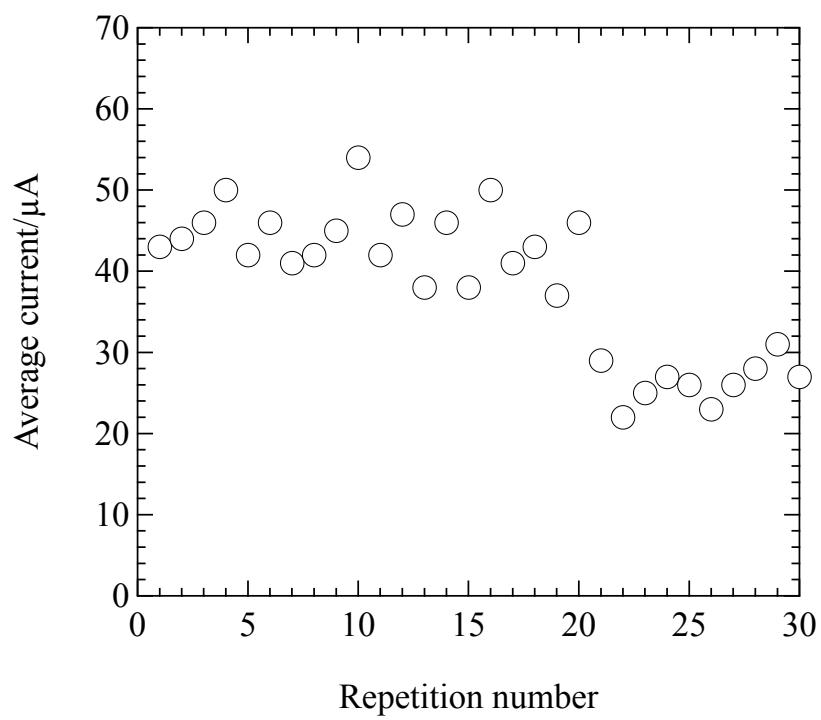


Fig. 2

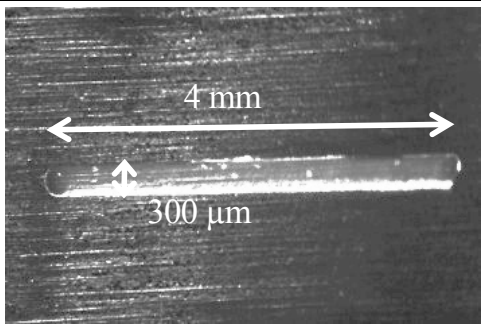
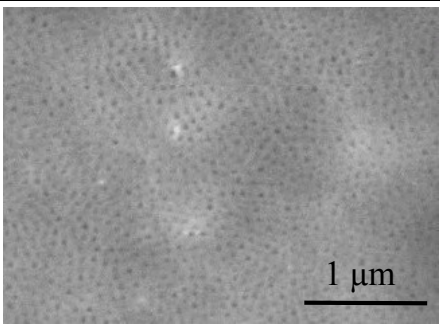
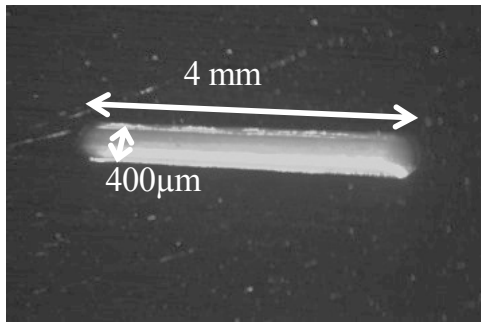
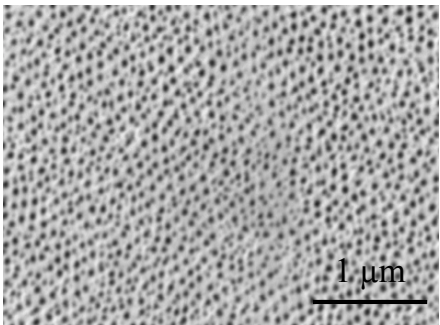
|                       | Optical Microscope                                                                 | SEM                                                                                 |
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| Repetition number: 30 |  |  |

Fig. 3

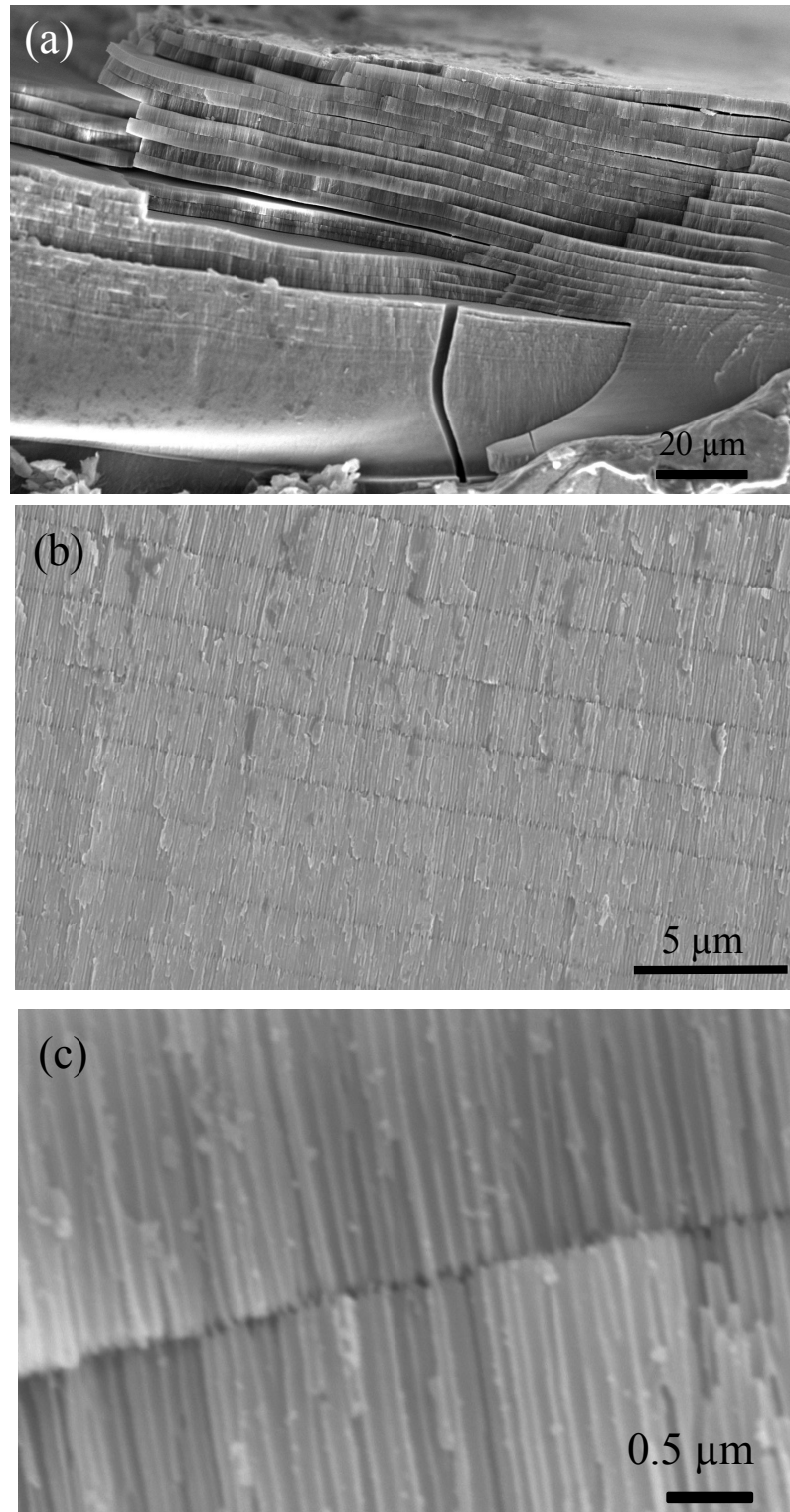


Fig. 4

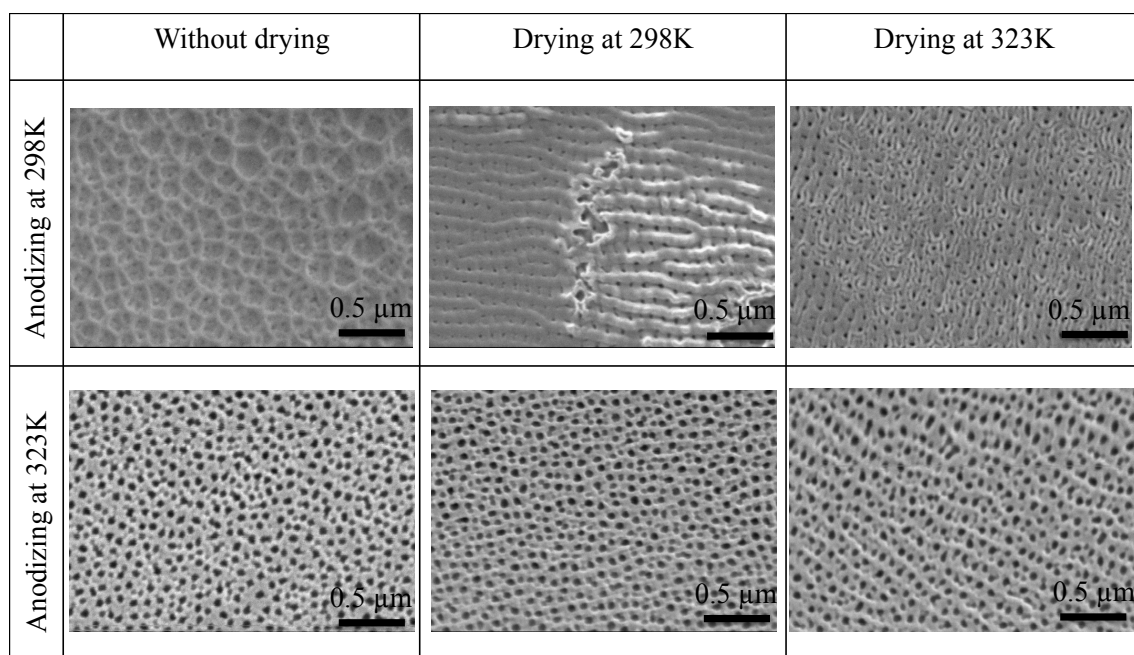


Fig. 5

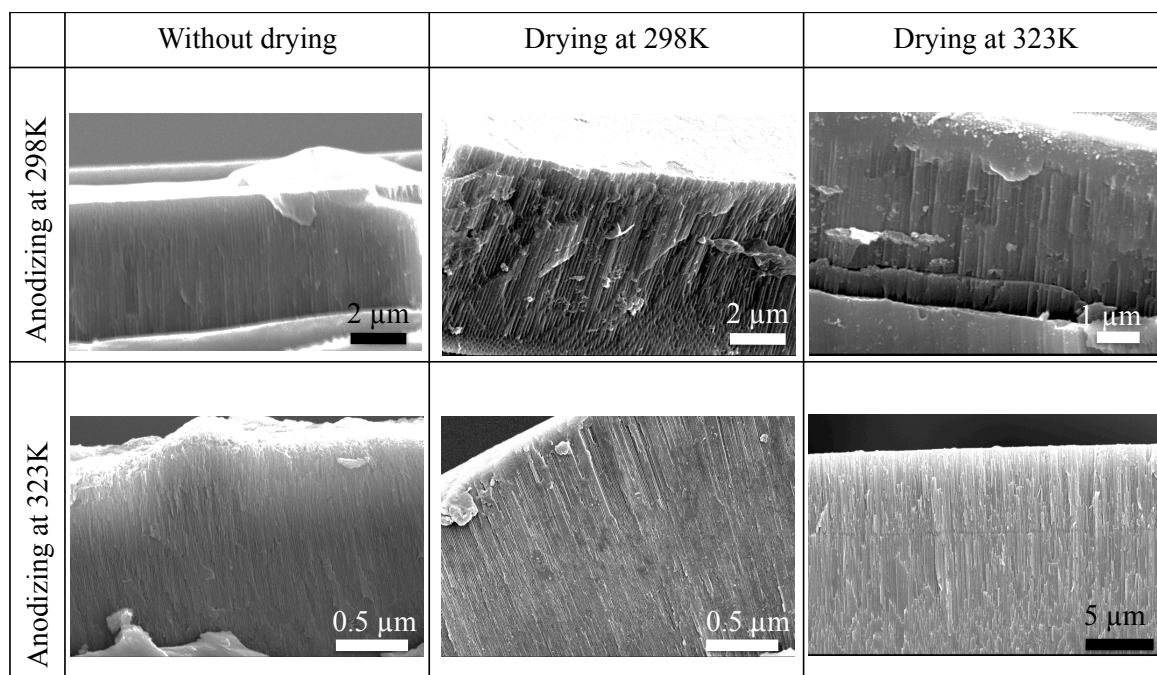


Fig. 6



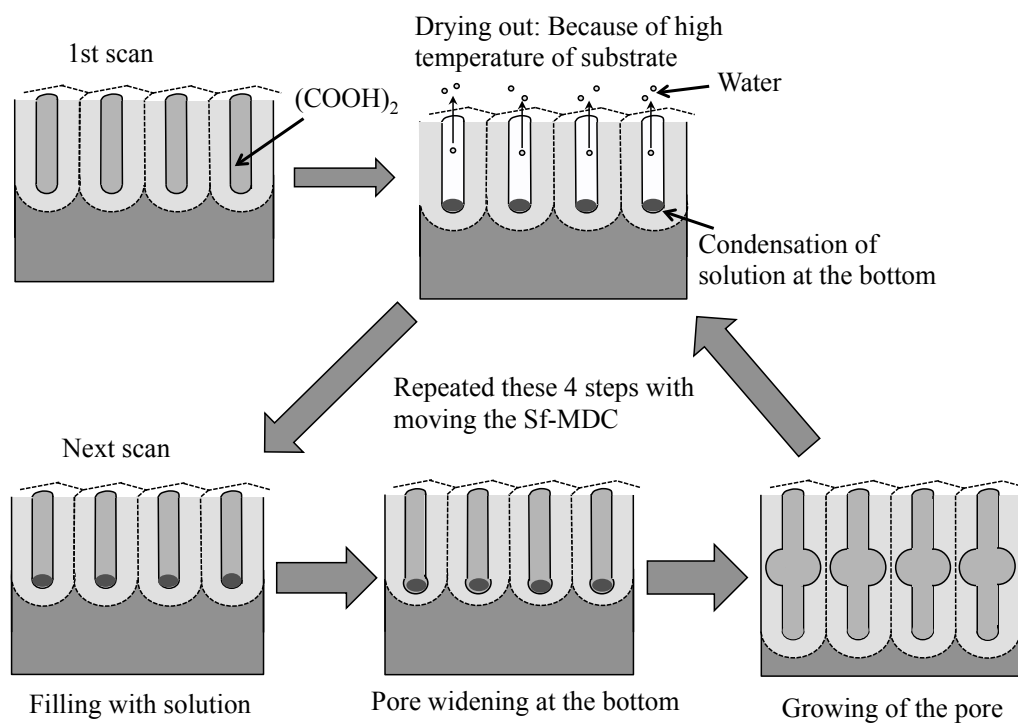


Fig.7