

# Structural and Electrical Properties of an Electrolyte-insulator-metal Device with Variations in the Surface Area of the Anodic Aluminum Oxide Template for pH Sensors

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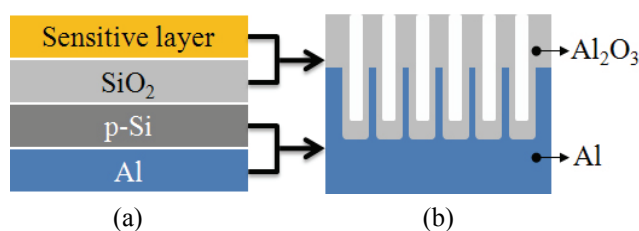
**Abstract** – In this study, we fabricated an electrolyte-insulator-metal (EIM) device incorporating a high-k  $\text{Al}_2\text{O}_3$  sensing membrane using a porous anodic aluminum oxide (AAO) through a two-step anodizing process for pH detection. The structural properties were observed by field-emission scanning electron microscopy (FE-SEM) and X-ray diffraction patterns (XRD). Electrochemical measurements taken consisted of capacitance-voltage (C-V), hysteresis voltage and drift rates. The average pore diameter and depth of the AAO membrane with a pore-widening time of 20 min were 123nm and 273.5nm, respectively. At a pore-widening time of 20 min, the EIM device using anodic aluminum oxide exhibited a high sensitivity (56mV/pH), hysteresis voltage (6.2mV) and drift rate (0.25mV/pH).

**Keywords:** Nanostructures, Electrochemical properties

## 1. Introduction

An ion-sensitive field effect transistor (ISFET) is an electrochemical sensor that reacts to ionic activity at the electrolyte/membrane interface of an exposed gate window [1]. When using sensing membranes such as  $\text{Si}_3\text{N}_4$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Ta}_2\text{O}_5$ , and  $\text{Sm}_2\text{O}_3$ , the ISFETs display near-Nernstian pH sensitivities. However, ISFET devices have some crucial drawbacks, such as poor adhesion and fast leaching-out of sensitive materials, as well as electrochemical corrosion of the passivation layer, and high fabrication costs due to the photolithographical process steps [2]. In contrast, capacitive electrolyte-insulator-silicon (EIS) is easy to manufacture and measure its characteristics, but is difficult to miniaturize, affecting the surface area of the sensor. In order to solve these problems, studies on changing the surface area have been conducted [3, 4]. However, ISFET and EIS devices have some disadvantages, such as drift, hysteresis and photosensitivity [5], which lower the accuracy of the sensor. High-k (high-dielectric constant) membranes can be considered as sensing membranes for application in ISFET and EIS devices. In general, high-k dielectrics, such as  $\text{Ta}_2\text{O}_5$ ,  $\text{HfO}_2$ , and  $\text{Al}_2\text{O}_3$  [6, 7], need to be thermally and chemically stable. In addition, they are required to have a large dielectric constant, small leakage current, and good interface quality [8].

In this study, we fabricated an electrolyte-insulator-metal (EIM) device using a porous anodic aluminum oxide (AAO) sensing membrane [9-11], which easily provides a



**Fig. 1.** Schematic diagram of (a) EIS device and (b) EIM device.

large surface area and improves sensitivity and stability. Fig. 1 shows a cross-sectional illustration of the EIS device and EIM device. In order to use EIS devices as electrochemical sensors, we should prepare metal electrodes at the bottom of the semiconductor part. On the other hand, the EIM structure can use the metal substrate directly as an electrode.

## 2. Experimental

High-purity aluminum foil (99.9995%, annealed, Alfa Aesar) specimens of  $1 \times 1 \text{ cm}^2$  with a thickness of 0.5mm were used as the substrate. Prior to anodization, the metal surfaces were degreased in ethyl alcohol for 30 min. They were electropolished in a solution of perchloric acid and ethyl alcohol (1:4 volumetric ratio) at 15V with 100  $\text{mA/cm}^2$ , and 10°C for 3 min. After electropolishing, the first step of the anodizing process was carried out in 0.04M oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) at 10°C, 80V for 1h. The AAO membrane was then removed by immersing the specimen in a mixture of 1.8 wt% chromic acid ( $\text{H}_2\text{CrO}_4$ ) and 6 wt% phosphoric acid ( $\text{H}_3\text{PO}_4$ ) at 65°C for 2h. Then, porous-type

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AAO films were obtained by carrying out the second anodizing step in an oxalic acid solution for 3 min. After the second anodizing step, the pores were widened by etching in a 5 wt% phosphoric acid solution at 45°C for 0-20 min.

The structure of the AAO substrate was analyzed by X-ray diffraction (XRD) with  $\text{CuK}\alpha$  emission. The surface and cross-sectional microstructures of the AAO membrane were examined using field-emission scanning electron microscopy (FE-SEM). The pH sensitivities of the EIM devices were determined by measuring the capacitance-voltage (C-V) curves. In order to measure the C-V characteristics, specimens were mounted in a home-made measuring cell sealed by an O-ring. The front side of the specimen was in contact with the electrolyte and an Ag/AgCl reference electrode (011464, BAS Inc.), and on the rear side with a gold-plated pin. An LCR meter (PM6306, Fluke) was operated at an ac signal magnitude of 50mV and frequency of 120Hz, and technical buffer solutions (Titrisol, Merck) of pH 3-11 were used. Hysteresis voltage and drift rate were measured using a voltage meter (Keithley 6517A).

### 3. Results and Discussion

Fig. 2 shows the XRD pattern of the anodic aluminum oxide membrane. The anodic aluminum oxide membrane showed the typical XRD pattern of a polycrystalline structure with the  $\gamma\text{-Al}_2\text{O}_3$  phase. This was confirmed by JCPDS card; 01-075-0921.

Fig. 3 and Fig. 4 show the surface and cross-sectional FE-SEM micrographs of AAO membranes by pore-widening time. By increasing the pore-widening time from 0 min to 25 min (Fig. 3(a) and 3(d)), the average pore diameter increased from 63nm to 158nm. However, the AAO membranes pore-widened for 25 min broke due to excessive etching. In the cross sectional FE-SEM micrographs of the AAO (Fig. 4), the upper parts of the AAO membrane were wider than the bottom portion. We expected these microstructures to display excellent

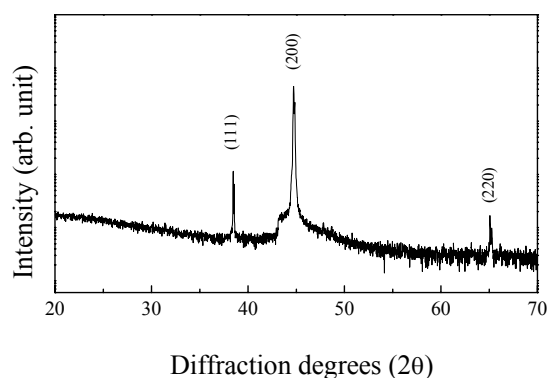


Fig. 2. XRD pattern of the anodic aluminum oxide membrane.

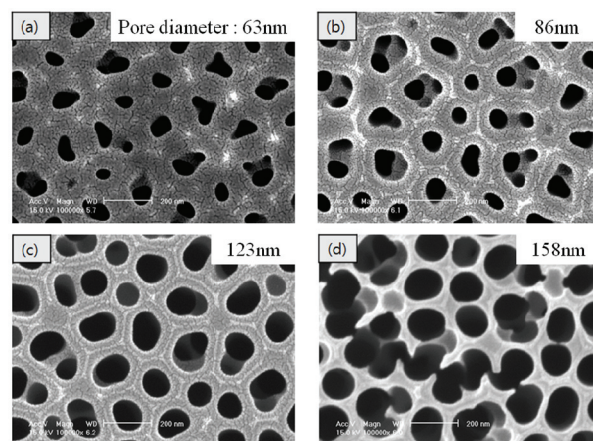


Fig. 3. Surface FE-SEM micrographs of AAO pore-widened for : (a) 0 min, (b) 10 min, (c) 20 min and (d) 25 min.

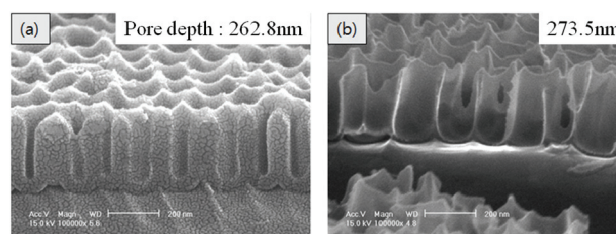
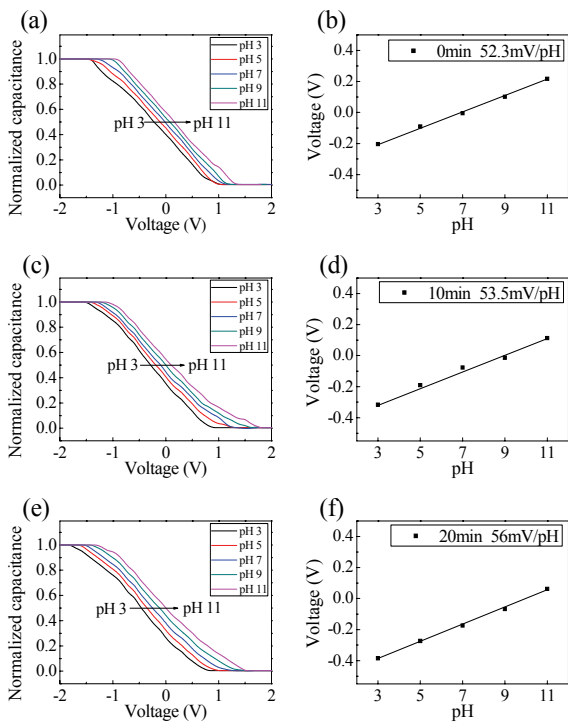


Fig. 4. Cross-sectional FE-SEM micrographs of AAO pore-widened for: (a) 0 min, and (b) 20 min.

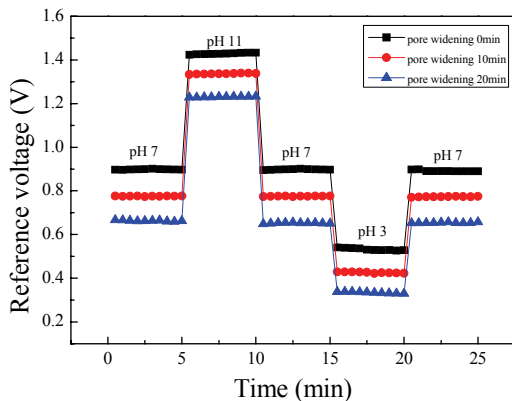
characteristics to detect liquid materials, due to the increase of the entrance and contact area. The thickness of the whole side of the  $\text{Al}_2\text{O}_3$  layer decreased during the pore-widening process. The average pore diameter and depth of the AAO membrane with a pore-widening time of 20 min were 123nm and 273.5nm, respectively.

Fig. 5 shows C-V curves for the EIS devices in different pH buffer solutions. The C-V curves were measured to determine the pH sensitivities of the sensing membrane. Varying the pH solution leads to the flat band voltage shift in the C-V curves. This behavior can be explained by considering the site-binding model [12]. The reference voltage was determined from the C-V curves to achieve the normalized capacitance of 0.5. The C-V curves shifted as a result of the surface potential modification by hydrogen ions. The AAO membrane with the pore-widening time of 20 min showed the highest sensitivity value of 56mV/pH, as shown in Fig. 5(f). The pH sensitivity increased with an increase in the surface area of the AAO membrane due to the increasing capacitance value of the measuring signal [13].

Fig. 6 shows the hysteresis behavior of AAO sensors at various pore-widening times. Hysteresis behavior was measured by immersing the prepared sensors in each pH standard solution for up to 5 min in a set cycle of pH 7→11→7→3→7. Despite an improvement in pH



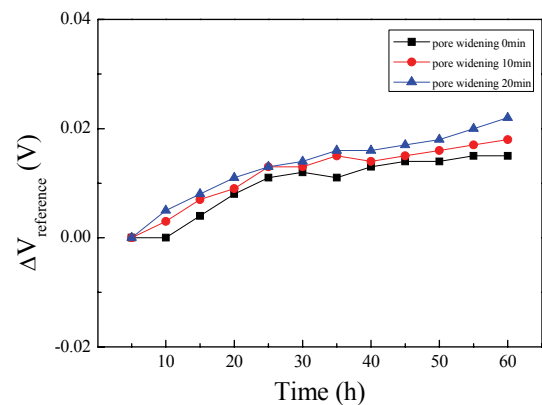
**Fig. 5.** Normalized C-V curves response of AAO membrane different pH buffer solutions, and pH sensitivity of the AAO membrane: pore-widening time (a), (b) 0min; (c), (d) 10 min; (e), (f) 20 min.



**Fig. 6.** Hysteresis voltage of AAO membrane at various pore-widening times

sensitivity, the hysteresis properties of the AAO membrane worsened slightly with an increase in pore-widening time. Hysteresis can be explained by defects in the insulator film. These responding sites respond to changes in the chemical composition of the solution in which the device is immersed, even though they are not located on the outer surface of the insulator. The responding site is located along the boundaries of grains on the insulator film [14].

Fig. 7 shows drift properties of AAO membranes at various pore-widening times at pH 7. The drift rate in the reference voltage of the EIS over a long time period poses a serious challenge in the widespread application of the



**Fig. 7.** Drift rates of AAO membranes at various pore-widening times at pH 7.

**Table 1.** Sensitivity, Hysteresis voltage, and Drift rates of AAO membranes at various pore-widening times.

Pore widening time (min)	Sensitivity (mV/pH)	Hysteresis voltage (mV)	Drift rate (mV/h)
0 min	52.3	6.2	0.34
10 min	53.5	6.5	0.29
20 min	56	6.8	0.25

solid-state pH sensor [15, 16]. Drift is known to increase slowly and monotonically with time when sensors are submerged in an electrolyte. Consequently, a higher drift rate is considered to be caused by a larger surface roughness, which indicates an increase in the possibility of the presence of defects in the dielectric material.

#### 4. Conclusion

We fabricated an AAO nano template using a two-step anodizing process. In addition, the sensing properties of hydrogen ions were investigated at various pore-widening times. The structure of the AAO substrate was analyzed by X-ray diffraction (XRD) with  $\text{CuK}\alpha$  emission and using field-emission scanning electron microscopy (FE-SEM). By increasing the pore-widening time from 0 min to 20 min (Fig. 3(a) and 3(c)), average pore diameter increased from 63nm to 158nm. The AAO membranes pore-widened for longer than 25 min broke due to excessive etching. The pH sensitivity, hysteresis voltage and drift rate of an EIM device at the pore-widening time of 20 min were 56mV/pH, 6.2mV and 0.25mV/pH, respectively.

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application of biosensor.

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