EFFECT OF CRYSTALLIZING CONDITION OF ANODIC ALUMINUM OXIDE MEMBRANE FOR pH SENSOR

Jin-Ho Yeo[1], Sung-Gap Lee[1,*], Hye-Rin Jung[1], Ye-Won Jo[1]
[1]Department of Ceramic Engineering, Engineering Research Institute
Gyeongsang National University, Jinju 660-701, Republic of Korea
jhyeo89@nate.com, lsgap@gnu.ac.kr[*]

ABSTRACT
In this study, we fabricated electrolyte-dielectric-metal(EDM) device incorporating a high-k Al_2O_3 sensing membrane through porous anodic aluminum oxide (AAO) by two step anodizing process for pH detection. To change the characters of the AAO template, the crystallizing time was varied from 0 hour to 10 hours at 600 ^oC. The structural properties were observed by field emission scanning electron microscopy (FE-SEM). The pH sensitivity increased in the crystallizing time from 0 hour to 2 hours and gradually saturated at 5 hours or more. The porous AAO sensor with the crystallizing temperature of 10 hours showed the good sensitivity and long-term stability were 54.1 mV/pH, 2.4mV/h, respectively.

KEY WORDS
Anodic Aluminum Oxide, capacitive EIS, Biosensor.

1. Introduction

In recent years, sensors based on semiconductor devices in combination with biological components have become highly attractive for both research and possible application in clinical diagnostics, environmental analysis, food quality control and forensics [1-3]. Ion-sensitive field-effect transistors (ISFETs) present a technology in which the common metal-oxide semiconductor field-effect transistor (MOSFET) gate electrode is replaced by an ion-sensitive surface to detect ion concentrations in solution [4]. When SiO_2 is used as the insulator (sensing membrane), the surface of the gate oxide contains –OH functionalities, which are in electrochemical equilibrium with ions in the solutions (H^+ and OH^-). The hydroxyl groups at the gate oxide surface can be protonated and deprotonated, and thus, when the gate oxide contacts an electrolyte solution, a change in pH will change the SiO_2 surface potential. Many different types of oxide coatings with inorganic materials, such as SiO_2, Si_3N_4, Al_2O_3 and Ta_2O_5, can be used to achieve a pH response and ISFETs show almost Nernstian pH sensitivities [5]. ISFETs have some advantages such as high sensitivity, micro size and the potential for on-chip circuit integration. However, this configuration has some crucial drawbacks, such as poor adhesion and fast leaching out of sensitive materials, as well as electrochemical corrosion of the passivation layer and the high cost of fabrication due to the photolithographic process steps [6].

To overcome these problems, many researchers suggest the application of a simple capacitive electrolyte-insulator-semiconductor (EIS) field-effect structure [7]. The layer set-up of this EIS sensor corresponds to the gate region of an ISFET. However, due to the missing photolithographic process steps, no additional passivation and encapsulation layer of the sensing area is necessary. Thus, this transducer structure possesses a higher stability in the long-term than ISFET-based transducer structures and allows cheaper and easier sensor preparation. In particular, the use of a dielectric layer Al_2O_3 as a pH-sensitive gate insulator for an EIS structure has been presented as a long-term stable pH sensor. However, miniaturization of capacitive EIS structures is very difficult since the scaling down of the active sensor area leads to a decrease in the measured capacitance.

In this work, a new concept for potentiometric Al-based sensors has been developed using an aluminum oxide layer as the transducer material for chemical sensors and biosensors.

Porous aluminum and aluminum oxide layers simultaneously formed by an anodic aluminum oxide (AAO) process without an additional deposition process. The enlargement of the active sensor area using a porous aluminum layer results in an increased capacitance value due to the measuring signal and improved sensitivity of the sensor. Due to this miniaturization, it is possible to combine several sensors into a multi-sensor array of the same chip size. We fabricated the capacitive EDM (electrolyte-dielectric-metal) sensor based on the AAO template, and investigated its electrochemical properties for application in chemical sensors.

2. Experimental

High-purity aluminum foils (99.9995 %, annealed, Alfa Aeser) with a thickness of 0.5 mm were used as the substrate. Anodic aluminum oxide (AAO) are fabricated as shown in Figure 1. Prior to anodization, the metal surfaces were degreased, etched in ethanol solution and rinsed in distilled water, and then electropolished to obtain a smooth surface. It was necessary to immerse the

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sample in concentrated perchloric acid solution for 5 minutes to remove the oxide layer formed during the electropolishing process. The first anodizing process was carried out in 0.04M oxalic acid at 10 ^{o}C for 6h under a constant voltage of dc 40 V. The first anodized layer was subsequently removed in a solution of chromic acid and phosphoric acid at 65 ^{o}C for 3h. The second anodizing process was carried ou in 0.04M oxalic acid at 10 ^{o}C for 3min a constant voltage of dc 40 V. After the second anodizing process, the pores were widened by etching in a 5 wt% phosphoric acid solution at 45 ^{o}C for 10min.

The AAO templates were characterized by using X-ray diffraction (XRD) and field-emission scanning electron microscopy (FE-SEM). For pH measurements, technical buffer solutions (Titrisol Merck) of pH 3-11 were used. In order to examine the potentiometric response of the sensors, the prepared samples can be easily mouted in a home-made measuring cell sealed by an O-ring. The sensor was contacted on its front side by the electrolyte and an Ag/AgCl reference electrode, and on the rear side by a gold-plated pin. To study the sensor characteristics, capacitance/voltage (C/V) measurements were taken with an LCR meter (Fluke 6306). These measurements were carried out at a dc voltage V_{bias} that was swept from 1 V to 5 V and a superimposed ac voltage with a frequency of 120 Hz and signal amplitude of 20 mV. The drift rate were measured using a voltage meter (Keithley 6517A).

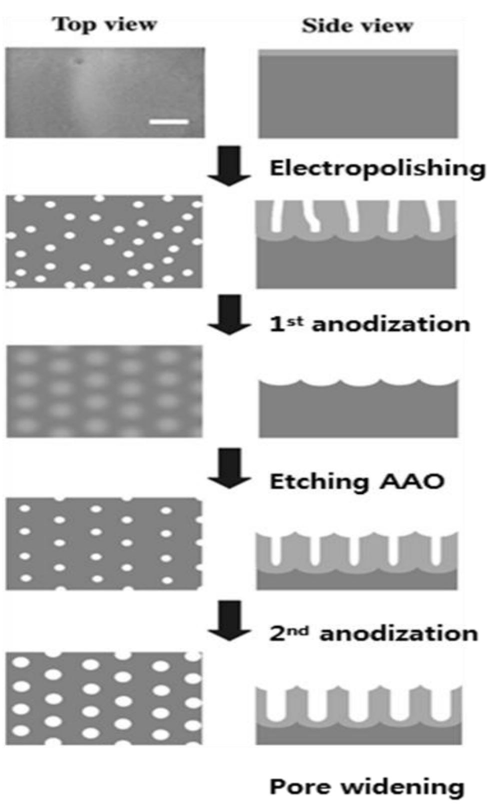

Figure 1. Schematic diagram of the process for the fabrication of anodic aluminum oxide (AAO) nanotemplate

3. Results and Discussion

In this study, the crystallizing time was varied from 0 hour to 10hours to enhance the sensitivity of the chemical sensor using the AAO material. Figure 2 and Figure 3 show the surface and cross-sectional FE-SEM micrographs of the AAO template. The pore size and thickness of the AAO template is not dependent on the crystallizing time; all specimens showed an average size of approximately 42nm and 151nm respectively.

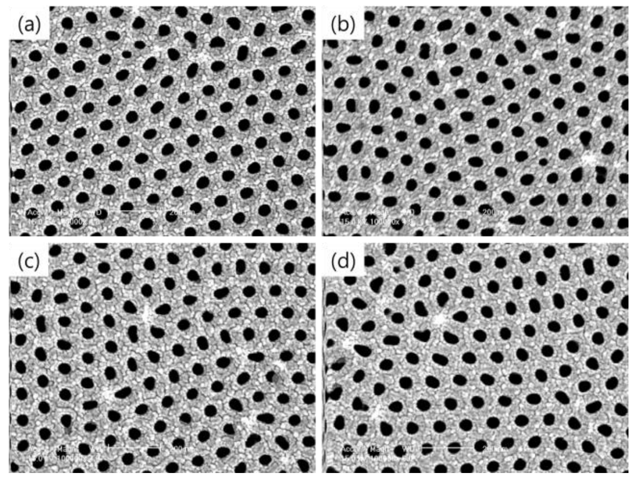

Figure 2. Surface FE-SEM micrographs of an AAO template at various crystallizing times:

(a) 0 hour, (b) 2 hours, (c) 5 hours, (d) 10 hours

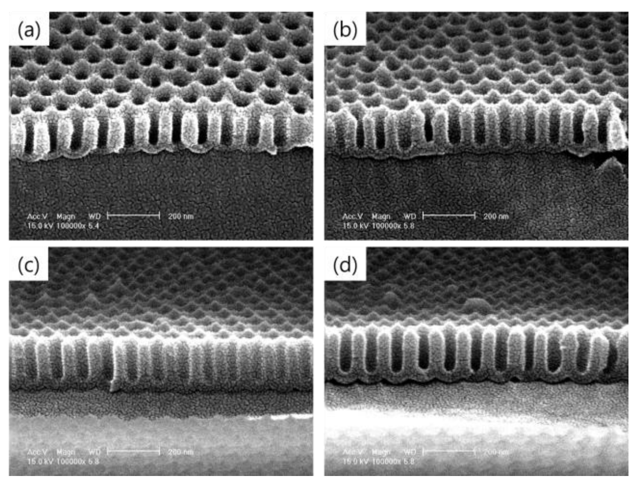

Figure 3. Cross-sectional FE-SEM micrographs of an AAO template at various crystallizing times:

(a) 0 hour, (b) 2 hours, (c) 5 hours, (d) 10 hours

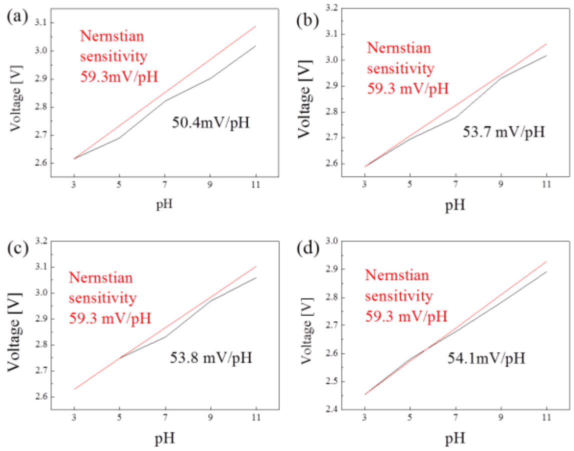

Figure 4. pH dependence of reference voltage and sensitivity of AAO-based EDM sensors at various crystallizing time:

(a) 0 hour, (b) 2 hours, (c) 5 hours, (d) 10 hours

Figure 4 shows the pH dependence of the reference voltages for EDM sensors. The reference voltage, which is described as the voltage for half-maximum normalized capacitance, was extracted from the C-V curves. The increased crystallizing time enabled by EDM structure using the AAO template improves not only the capacitance, but also the pH sensitivity of the sensors. The sensor with the crystallizing time of 10 hours, i.e., the AAO thickness of 151 nm, showed the highest value of 54.1 mV/pH, which is very close to the theoretical Nernstian slope of 59.3 mV/pH under standard conditions. These fundamental investigations demonstrate the suitability of the porous EDM structure using an AAO template as potentiometric pH sensors. The effect of the crystal structure of the EDM sensor on the improved pH sensitivity has been successfully explained by the surface-binding model [8].

4. Conclusion

In this paper, we studied the structural and sensing properties of a new concept for potentiometric AAO-based EDM (electrolyte-dielectric-metal) sensors to be used as chemical sensors and biosensors. It was found that, within the experimental conditions explored, all XRD peaks of the AAO template are consistent with those of a polycrystalline structure γ-Al2O3. The pore size of the AAO template, thickness, pH sensitivity and long-term stability of sensors with a crystallizing time 10 hours were approximately 42nm, 151 nm, 54.1 mV/pH and 2.4 mV/pH, respectively. This can be explained by the increase in the effective crystalline property. Capacitive EDM sensors based on an AAO template show promise for use in biomedical engineering applications.

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