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# Sensing performance of electrolyte-insulator-metal device based anodic aluminum oxide for pH detection

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We fabricated the electrolyte-insulator-metal (EIM) sensor on the base of anodic aluminum oxide (AAO) template for capacitive pH sensors. For the change of the thickness of AAO template, the second anodizing time was varied from 1 min to 10 min. With increasing the second anodizing time from 1 min to 10 min, the thickness of AAO template increased from 90 nm to 1.3  $\mu$ m. And the surface area compared to planar structure increased from 3 times to 25 times. The pH sensitivity of sensors with the second anodizing time of 10 min showed the highest value of 56.8 mV/pH in the concentration range from pH 3 to pH 11, a large hysteresis voltage of 7.6 mV in a cycle of pH 7  $\rightarrow$  11  $\rightarrow$  7  $\rightarrow$  3  $\rightarrow$  7. The EIM sensor with the second anodizing time of 1 min exhibited the best long-term stability of 2.5 mV/h.

Key words: AAO, EIM, pH sensors.

#### Introduction

In recent years, sensors based on semiconductor devices in combination with biological components have been highly attractive for both research and possible application in clinical diagnostics, environmental analysis, food quality control and forensic application [1-3]. Ion sensitive field effect transistor (ISFET) offers a technology by which the common metal oxide semiconductor field effect transistor (MOSFET) gate electrode is replaced by ion sensitive surface to detect ion concentration in solution [4,5]. ISFETs have some advantages of high sensitivity, microsize and potential for on-chip circuit integration. But, this configuration have some crucial drawbacks, such as poor adhesion an fast leaching-out of the sensitive materials as well as electrochemical corrosion of the passivation layer and high costs of fabrication due to photolithographical process steps [6].

To overcome these problems, many researchers suggest the application of a simple capacitive electrolyte-insulatorsilicon (EIS) [7]. 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 is cheaper and easier in sensor preparation]. Especially, dielectric layer of Al<sub>2</sub>O<sub>3</sub> as pH-sensitive gate insulator for EIS structure has been presented as a long-term stable pH sensor. But, miniaturization of capacitive EIS structures is very difficult since the scaling down of the active sensor area leads to decreasing of the measured capacitance.

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

Porous aluminum and aluminum oxide layer were simultaneously formed by an anodic aluminum oxide (AAO) process without additional deposition process. The enlargement of the active sensor area using porous aluminum layer results in increased capacitance value as the measuring signal and improved sensitivity of the sensor. We fabricated the capacitive EIM (electrolyteinsulator-metal) sensor on the basis of AAO template, and investigated the electrochemical properties for application in chemical sensors.

## Experimental

High purity aluminum foils (99.9995%, Alfa Aeser) with a thickness of 0.5 mm were used as substrate. Prior to anodization, the metal surfaces were degreased, etched in ethanol solution and rinsed in distilled water, then electropolished to obtain a smooth surface. It was necessary to immerse the sample in concentrated perchloric acid solution for several minutes to remove the oxide layer formed during the electropolishing process. The first anodizing process was carried out in a 0.04 M oxalic acid at 10 °C for 1 hr under a constant voltage of dc 80 V. The first anodized layer was subsequently removed in a solution of chromic acid and phosphoric acid at 65 °C for 2 hrs. The second anodizing process was then carried out under various anodizing times in the range of 1-10 min over fixed voltage and temperature as the first step. After second anodizing process, the pores are widened by etching in

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a 5 wt% phosphoric acid solution at 45 °C for 20 min.

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 Merk) of pH 3-11 were used. The sensor was contacted on its front side by the electrolyte and an Ag/AgCl reference electrode, on the rear side by a gold-plated pin. To study the sensor characteristics, capacitance/voltage (C/V) measurements were performed with LCR meter (Fluke 6306). These measurements were carried out at a dc voltage which was swept from -2 to 1 V and a superimposed ac voltage with frequency 120 Hz and signal amplitude of 20 mV. The hysteresis voltage and drift rate were measured using voltage meter (Keithley 6517A).

#### **Results and Discussion**

The typical XRD patterns of AAO is shown in Fig. 1, in which all peaks are consistent with those of a polycrystalline structure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (JCPDS No. 01-075-0921). The peaks in the XRD pattern are rather sharp, which indicate relatively high crystallinity of the membrane. The average crystal size of AAO was estimated to be about 43 nm from the broadening of the corresponding XRD peaks using the Scherrer formula [8].

Generally, the thickness of AAO template varies according to the second anodizing time. In this study, the second anodizing time was varied from 1 min to 10 min to enhance the sensitivity of the chemical sensor using the AAO material. Fig. 2 shows the surface and cross-sectional FE-SEM micrographs of AAO template. The pore size of AAO template is not shown a dependence on the second anodizing time, all specimens showed the average pore size of approximately 120-140 nm. But with increasing the second anodizing time from 1 min to 10 min, the thickness of AAO template increased from 90 nm to 1.3  $\mu$ m. And the surface area compared to planar structure increased from 3 times to 25 times. The thickness of barrier layer decreased with an increase the second anodizing time.



Fig. 1. XRD patterns of the anodic aluminum oxide template.



**Fig. 2.** FE-SEM micrographs of AAO template with variation of the second anodizing time: (a), (c) surface and (b), (d) cross-sectional morphologies.



**Fig. 3.** Normalized C-V curves of AAO-based EIM sensors in the buffer solutions from pH 3 to pH 11 with variation of the second anodizing time: (a) 1 min, (b) 3 min, (c) 5 min, and (d) 10 min. The insets show the pH dependence of reference voltage and sensitivity of AAO-based EIM sensors.

Fig. 3 shows a typical set of normalized C-V curves of EIM sensors as the pH transducer in the concentration range from pH 3 to pH 11. The C-V curves were obtained by sweeping voltages at the backsides contact and setting the reference electrode as a ground in several different pH solutions. The parallel shift of the C-V curves is caused by the flat-band voltage shift due to the pH change in the solutions. This shift can be explained by the variation of the ionization states of the  $Al_2O_3$  surface groups, described in the site-binding theory [9].

The inset of Fig. 3 shows the pH dependence of reference voltages for EIM sensors. The reference voltage, which is described as a voltage for half maximum of the normalized capacitance, was extracted from C-V curves. The increased surface area enabled by EIM structure improves not only the capacitance, but also the pH sensitivity of sensors. The sensor with the



**Fig. 4.** (a) Hysteresis voltage and (b) drift rates in a pH 7 buffer solution of AAO-based EIM sensors with variation of the second anodizing time.

second anodizing time of 10 min, i.e., AAO thickness of  $1.3 \,\mu\text{m}$ , showed the highest value of 56.8 mV/pH, which is very close to the theoretical Nernstian slop of 58 mV/pH at standard conditions. These fundamental investigations demonstrate the good suitability of the porous EIM structure using AAO template as potentiometric pH sensors. The effect of the increased in the surface area of EIM sensor on the improved pH sensitivity has been successfully explained by the surface-binding model [10].

Fig. 4(a) shows the hysteresis voltage for EIM sensors measured by immersing the prepared sensors in each pH standard solution for up to 5 min in a set cycle of pH 7  $\rightarrow$  11  $\rightarrow$  7  $\rightarrow$  3  $\rightarrow$  7. The hysteresis voltage here is defined as a difference between the initial reference voltage and the final reference voltage measured in the above cycle. Despite an improvement in the pH sensitivity with increased the thickness of AAO template, the hysteresis properties of the EIM sensors became slightly worse with thicker. Hysteresis phenomenon is known to be related to chemical interaction between ions in an electrolyte and the surface defects of the membrane [11]. The surface roughness increased with an increase in AAO template thickness, an increase in the second anodizing time. Consequently, it is expected that larger surface area should contain more surface defects or slow reacting surface-sites. The interior sites of these porous defects could react with the ions existing in the electrolyte solution and thus causes hysteresis response.

Fig. 4(b) shows the drift characteristics of EIM sensors with the variation of the second anodizing time measured in the pH 7 buffer solutions for 60 h at RT.

The drift is known to increase slowly and monotonically with time when sensors are submerged in electrolyte. The hydration of the dielectric and the diffusion of ions in electrolyte to the dielectric, i.e., the changes in the chemical composition of the dielectric surface, are attributed to cause the drift effect. Consequently, a higher-drift rate was considered to be caused by a larger surface roughness which indicates an increase the possibility of the presence of defects in the dielectric material. The EIM sensor with the second anodizing time of 1 min exhibited the best long-term stability of 2.5 mV/h.

## Conclusions

We studied the structural and sensing properties of a new concept for potentiometric AAO-based EIM sensors for chemical sensors and biosensors. It was found that, within the experimental conditions explored, all XRD peaks of AAO template are consistent with those of a polycrystalline structure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The thickness of AAO template, pH sensitivity and hysteresis voltage of sensors with the second anodizing time of 10 min were about 1.3 µm, 56.8 mV/pH and 7.6 mV, respectively. This can be explained by the increase of the effective surface area of the sensor. The capacitive EIM sensors on the basis of AAO template show promise for use in biomedical engineering applications.

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