

Electrochemical properties of porous electrolyte-insulator-metal device based anodic aluminum oxide template

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We fabricated the Si_3N_4 film-coated anodic aluminum oxide (AAO) template for chemical sensors. The average depth and diameter of pores were increased with increasing the second anodizing time and pore widening time, respectively. The average depth of pores of AAO template with the second anodizing time of 10 min was about 1.49 μm . The porous AAO sensor with the second anodizing time of 10 min and pore widening time of 15 min showed the highest capacitance of 142.92 nF. The capacitance increased in the pore widening time from 0 min to 10 min and gradually saturated at 15 min or more. The porous AAO sensor with the second anodizing time of 10 min and pore widening time of 10 min showed the good normalized C-V properties, and the pH sensitivity and the set values of the capacitance, working point, of these devices were 0.63 V, 0.27 V, 53.6 mV/pH and 48.2 mV/pH, respectively.

Key words: Anodic Aluminum Oxide, Capacitive EIS, Biosensor.

Introduction

The need of structure which has nanometre-scale patterns has increasing by decreasing the size of electronic devices and highly integrating. For satisfying this demand, the nanotechnology which can deal the nanometre size dot or wire is required. One of the most common nanotechnology is anodic aluminium oxide (AAO) [1-4] template method. It is advantage which the pore size and the interval between pores can be easily controlled by appropriately anodizing conditions, such as electrolyte, voltage, time and temperature etc. And also, AAO template itself has advantages such as various morphological properties and good chemical and thermal stability properties [5, 6].

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. [7] 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 of pH will change the SiO_2 surface potential. Many different types of oxide coatings of inorganic materials, such as SiO_2 , Si_3N_4 , Al_2O_3 and Ta_2O_5 , can be used for obtaining a pH response and the ISFET show almost Nernstian pH sensitivities.⁸⁾ ISFETs have some crucial drawbacks, such as poor adhesion a 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 [9]. To overcome these problems, many researchers suggest the application of a simple capacitive electrolyte-insulator-silicon (EIS) field-effect structure.¹⁰⁾ And this transducer structure possesses a higher stability in the long-term than ISFETs structure and is cheaper and easier in sensor preparation. In this study, we fabricated the electrolyte-insulator-metal (EIM) sensors by using an AAO template, which is easy to control the surface structure, and investigated the structural and electrical properties for application in chemical sensors.

Experimental

The AAO templates were fabricated by two steps anodizing processes. Aluminum foil (99.999%, Alfa Aesar) specimens of $1 \times 1 \text{ cm}^2$ with the thickness of 0.5 mm were prepared. The specimens were electro-polished at 20 V with 100 mA/cm² in a mixed solution of perchloric acid and ethanol at 10 °C for 5 min. The specimen was used as an anode, while an alumina plate coated with Pt was used as a cathode. After electro-polishing, the first anodizing process was carried out in an oxalic acid solution for 1 h. The AAO layer was then removed by immersing the specimen in a mixture of 1.8 wt% chromic acid and 6 wt% phosphoric acid at 65 °C for 3 h. And then porous-type AAO films were obtained by the second anodizing step carried out in an oxalic acid solution. The pores are widened by etching in a 5 wt% phosphoric acid solution at 45 °C. In order to obtain an AAO template having a various surface area, the specimens were fabricated with variation of the second anodizing time as 1, 3, 5, 10 min and pore

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widening time as 0, 5, 10, 15 min. Generally, the second anodizing time does not affect the pore diameter, but only affect the depth of AAO template. Si_3N_4 film, which used as the sensing layer of sensor devices, was deposited by enhanced chemical vapor deposition (PECVD) method.

The surface and cross-sectional microstructures of Si_3N_4 film-coated AAO template were examined using field-emission scanning electron microscopy (FE-SEM). The capacitance of Si_3N_4 /AAO templates was investigated using LCR meter (PM6306, Fluke). In order to examine the electrochemical properties, the specimens were mounted in a home-made measuring cell sealed by an O-ring. The specimen was contacted on its front side by the electrolyte and an Ag/AgCl reference electrode (011464, BAS Inc), on the rear side by a gold-plated pin. For pH measurements, technical buffer solutions (Titrisol Merk) of pH 4-10 were used. And for verify the potential to chemical sensor the voltage was investigated with various pH solution using Data acquisition/Switch unit (34970A, Agilent).

Results and Discussion

Fig. 1 shows the cross-sectional FE-SEM micrographs of AAO templates with variation of the second anodizing time. The pore widening time was fixed to 15 min. The average depth of pores increased from about 112 nm to 1.49 μm with an increase in the second anodizing time from 1 min to 10 min. The thickness of barrier layer decreased with increasing the second anodizing time, and many channels grew irregularly due to the sub-holes.

Fig. 2 shows the surface FE-SEM micrographs of AAO templates with variation of pore widening time. The second anodizing time was fixed to 1 min. The disordered pores of AAO and the dense barrier layer were shown in Fig. 2(a). The average diameter of pores increased from about 107 nm to 169 nm with an increase in pore widening time from 0 min to 15 min. Additionally, the pore size and the thickness of walls not uniform, and many sub-holes appeared adjacent to the main holes, as shown in Fig. 1.

Porous silicon (Si) has recently been discussed as a

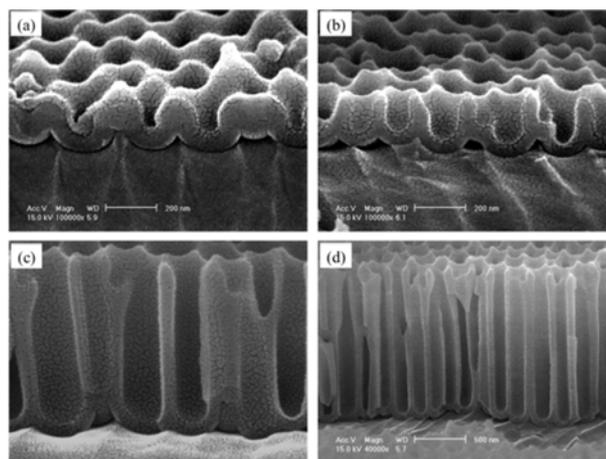


Fig. 1. Cross-sectional FE-SEM micrographs of AAO templates with variation of the second anodizing time: (a) 1 min, (b) 3 min, (c) 5 min and (d) 10 min.

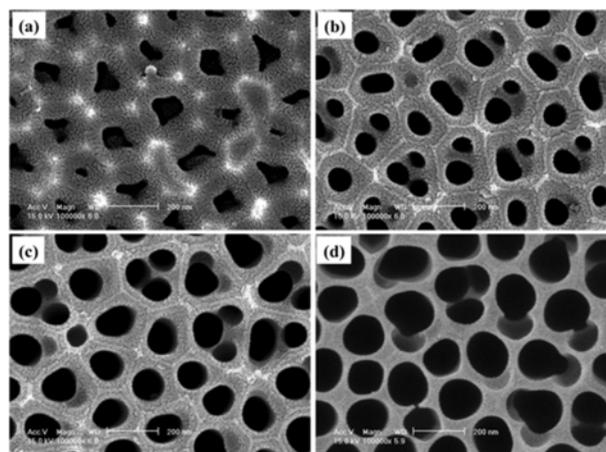


Fig. 2. Surface FE-SEM micrographs of AAO templates with variation of pore widening time: (a) 0 min, (b) 5 min, (c) 10 min and (d) 15 min.

substrate material for capacitive chemical sensors and biosensors [11, 12]. The use of porous instead of planar silicon as substrate material provides many advantages. Due to the surface area increases, also the capacitance value as the measuring signal raises and consequently, a scaling down of the porous sensor towards a porous

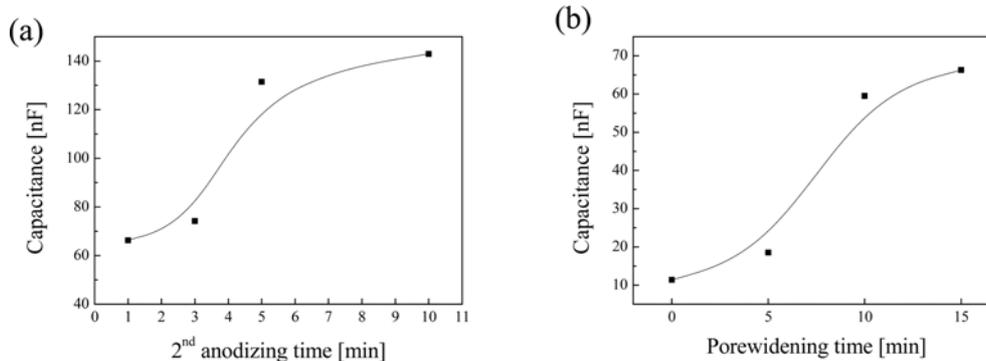


Fig. 3. Capacitance of AAO sensor with variation of (a) the second anodizing time and (b) pore widening time.

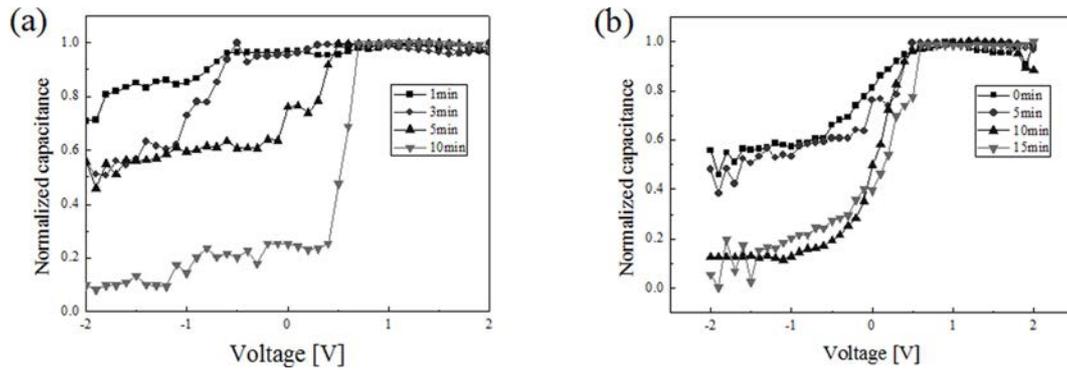


Fig. 4. Normalized capacitance-voltage (C-V) characteristics of AAO sensor with variation of (a) the second anodizing time and (b) pore widening time.

micro-sensor is feasible. In this work, a new approach is presented that capacitive EIM chemical sensor by using an AAO template as a transducer material was fabricated. Fig. 3(a) and (b) show the capacitance of AAO sensor with variation of the second anodizing time and pore widening time, respectively. The capacitance increased with an increase the second anodizing time and pore widening time due to increase the surface area of AAO template. If each channel is assumed to straightly grow with the uniform wall, the surface area of porous AAO template increased to 13 times with increasing the second anodizing time from 1 min to 10 min. However, the measured capacitance did not show a proportional increase in the second anodizing time or surface area of porous AAO template. These properties can be understood in terms of the effect of non-uniform channel due to sub-holes and the coupling between adjacent channels, as shown in Fig. 1 and 2. The capacitance increased in the pore widening time from 0 min to 10 min and gradually saturated at 10 min or more. This suggests that the partially merging between adjacent pores occurred with increasing the pore diameter, as shown in Fig. 2. The porous AAO sensor with the second anodizing time of 10 min and pore widening time of 15 min showed the highest capacitance of 142.92 nF.

The electrical double layers at the oxide/solution (electrolyte) interfaces have been studied extensively [13-15]. It is generally considered that the surface charging mechanism for oxides is the adsorption of protons or hydroxyl ions by surface hydroxyl groups to form positive or negative sites, respectively. Especially, it is known that the surface of Si_3N_4 , Ta_2O_5 and Al_2O_3 films contains hydroxyl groups, the dissociation degree of which depends on the solution pH and contributes to a pH-dependent surface potential. The potential drop across the electrical double layer depends on both the surface charge distribution and dipole moments of the interfacial ion pairs [16]. Fig. 4(a) and (b) show the normalized capacitance-voltage (C-V) characteristics of AAO sensor with variation of the second anodizing time and pore widening time, respectively. C-V measurements were performed with a LCR-meter at a dc voltage which was swept from -2 V to 2 V in steps on 100 mV and a superposed ac

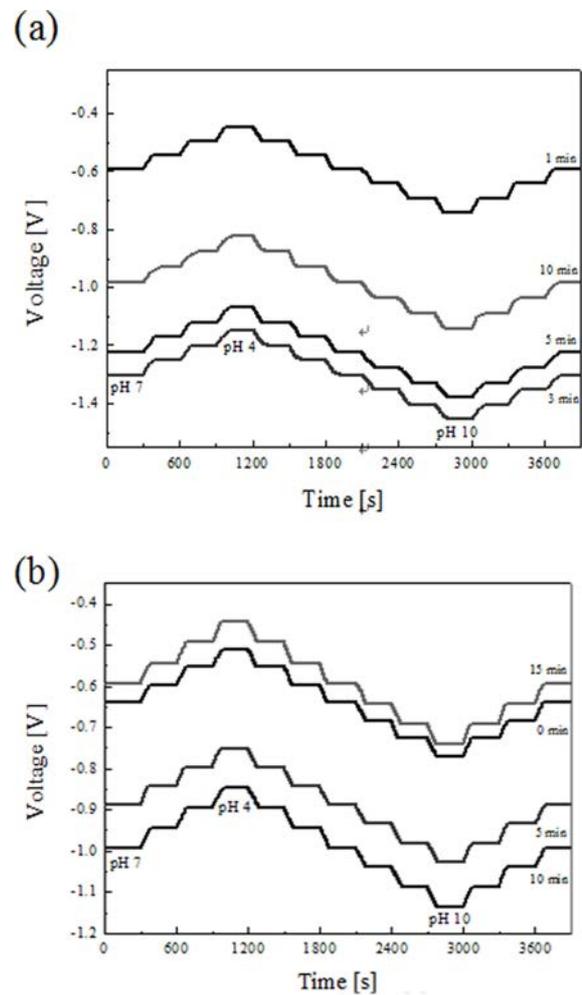


Fig. 5. Hysteresis behaviour of AAO sensors with variation of (a) the second anodizing time and (b) pore widening time.

voltage with a frequency of 120 Hz and a signal amplitude of 50 mV . The difference of normalized capacitance between the maximum and minimum values increased with an increase the second anodizing time and pore widening time, similar to the capacitance properties shown in Fig. 3. The C-V curves have a linear shape, which guarantees that only the concentration-dependent potential shift as resulting chemical sensor is measured [17]. Therefore, the change of

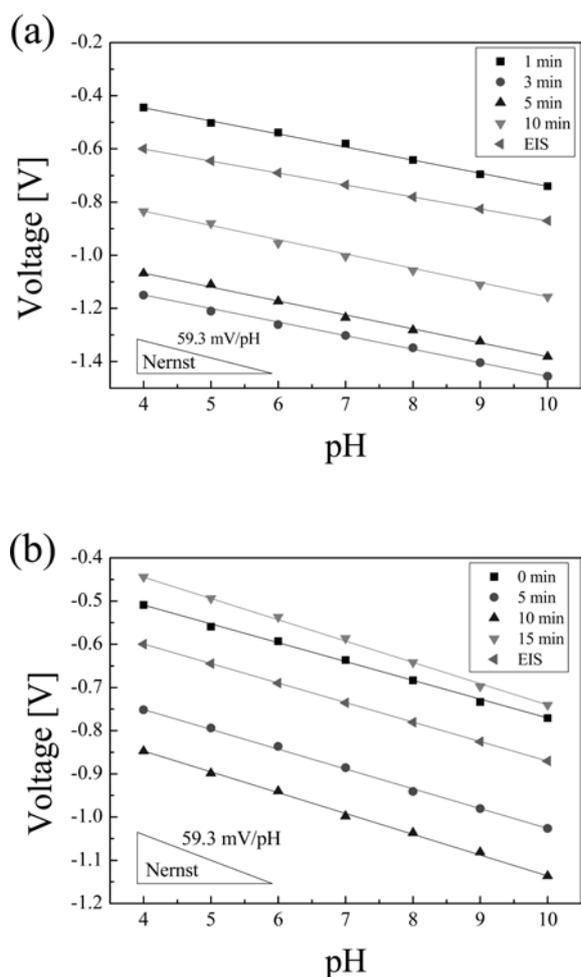


Fig. 6. Calibration curve (pH vs. voltage) of AAO sensors with variation of (a) the second anodizing time and (b) pore widening time.

capacitance value at the linear region corresponds to the pH-sensitivity property of AAO sensor. The porous AAO sensor with the second anodizing time of 10 min and pore widening time of 10 min showed the good normalized C-V properties, and the set values of the capacitance, working point, of these devices were 0.64 V and 0.27 V, respectively.

Fig. 5(a) and (b) show the hysteresis behaviour of AAO sensors with variation of the second anodizing time and pore widening time, respectively. The measurement of hysteresis behaviour was performed by immersing the prepared sensors in each pH standard solution for up to 5 min in a set cycle of pH 7 pH4 pH10. However, the hysteresis properties of porous AAO sensors became worse with increasing the second anodizing time and pore widening time. This is because the larger surface area should contain more surface defects or slow reacting surface sites. The interior sites of these surface defects could react with the ions existing in the electrolyte solution [19].

Fig. 6(a) and (b) exemplarily present the typical calibration curve within the concentration range from pH4 to pH10 of AAO sensors with variation of the second

anodizing time and pore widening time, respectively. The pH sensitivity of AAO sensors increased with an increase the second anodizing time and pore widening time due to the increase in the surface area of AAO template [18]. The pH sensitivities with variation of the second anodizing time and pore widening time were approximately 49 to 53 mV/pH and 45 to 49 mV/pH, respectively. As can be seen from the calibration curve in Fig. 6(a), for the second anodizing time of 10 min the highest pH sensitivity of 53.8 m/pH, which is close to the theoretical Nernstian slope of 59.3 mV/pH at standard conditions, was achieved. M. J. Schoning [10] have reported a sensitivity property of 45.1 mV/pH in EIS structure coated with Si_3N_4 as a sensing material. Therefore, EDM structure with porous substrate presented the excellent sensitivity characteristic than the plate-EIS structure.

Conclusions

Si_3N_4 film coated-AAO templates were fabricated with variation of the second anodizing time and pore widening time. The structural and electrochemical properties were observed for application as chemical sensors. With increasing the second anodizing time and pore widening time, pores and channels grew irregularly due to the sub-holes. The capacitance increased in the pore widening time from 0 min to 10 min and gradually saturated at 10 min or more. The pH sensitivity of AAO sensors increased with an increase the second anodizing time and pore widening time due to the increase in the surface area of AAO template. However, the hysteresis properties of porous AAO sensors became worse with increasing the second anodizing time and pore widening time. Because the larger surface area should contain more surface defects or slow reacting surface sites.

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