

DEVELOPMENT OF NANOPOROUS AAO BASED CAPACITIVE-TYPE SENSORS FOR HEAVY METAL ION (ARSENIC) SENSING APPLICATION

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In this work the evolution of a capacitive type sensor based on nanoporous anodic aluminum oxide (AAO) fabricated by a two-step anodization process using a low-cost customized setup designed in-house is reported. The parallel plate capacitors were fabricated using aluminum (Al) as base electrode and gold as top electrode, where the porous AAO was used as the dielectric material. This demonstrated the clear dependence of the capacitance values of the as prepared different sensors on the dielectric material's thickness. The as developed sensors were tested for the detection of arsenic (As) ions. An increase in the capacitance was observed while increasing the concentration of the As ion in aqueous solutions. The presence of As ion was confirmed through EDS (Energy dispersive X-ray spectroscopy) mapping carried out in a FESEM. This change in capacitance can be attributed to the change in dielectric constant of the active material with the incorporation of metal ions.

Keywords: *Capacitive-type sensor; Nanoporous Anodic Aluminum Oxide (AAO); Anodization; Energy dispersive X-ray spectroscopy (EDS)*

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1. INTRODUCTION

Self-organized, highly ordered nanopores in Anodic Aluminum Oxide (AAO) with high periodicity and density distribution have found widespread use in a variety of nanoscale applications [1,2]. In addition to its promise as a template for the growth of other nanostructured materials, AAO's increased surface area due to the uniform arrangement of ordered nanopores is showing promising results in the development of sensors. Due to its increased uniform nanoporous surface area that enhances the water adsorption capacity [3,4,5], AAO has been reported as a useful material for the fabrication of capacitive humidity sensors, pressure sensors, and bacteria sensors by a number of researchers [4-9]. Capacitive type sensors are rising in popularity among the many existing sensor types (capacitive, resistive, mass-sensitive, electromagnetic, etc.) due to their improved sensitivity and simpler fabrication procedure [10]. Numerous nanoporous AAO-based capacitive humidity sensors have been reported to date [5-9]. The widespread contamination of ground water supplies with arsenic has been labeled a modern environmental catastrophe [11-14]. Direct detection of As (III) in ground water using spectroscopic methods is challenging because of its low concentration. Taking advantage of their large surface area, AAO nanopores can be modified to detect a variety of metal ions. For the selective extraction of trace arsenite ions, AAO is used as it is a highly sensitive material [15]. Capacitive type sensors based on AAO have demonstrated excellent sensing of As ions in ground water [15]. AAO can be made using a number of different fabrication methods, including sputtering, sol gel process and Chemical Vapor Deposition (CVD). However, these techniques call for high-end equipment, which drives up costs. However, the electrochemical anodization technique has been proved as a simple and cost-effective process, where the different parameters involved in the fabrication process such as thickness, porosity etc. can be controlled easily [16].

This work describes the development of a AAO based capacitive type sensor using a conventional two-step anodization method starting with a low cost commercially available aluminum alloy. Since the thickness of the dielectric material has an inverse relationship with the capacitance of a parallel plate capacitor, we have emphasized here to develop a thicker AAO layer within a short interval of time. For this purpose, the hard anodization method is involved as it has been proved as a fast fabrication method. The sensing of arsenic ion using the as developed AAO based capacitive type sensor is reported here.

2. MATERIALS AND METHODS

Commercially available aluminum sheet was used for the experiments. The 0.5 mm thick aluminum sheet was cut into required sizes for anodization. Prior to anodization, the aluminum sheets were ultrasonically cleaned in a mixture of acetone and deionized water for 10 minutes and annealed at 250°C for 4 hours. To dissolve the naturally occurring oxide coating the aluminum sheets were electropolished in a solution mixture of H₃PO₄, H₂SO₄ and deionized water with 2:2:1 weight ratio respectively. The aluminum sheets were then washed several times with deionized water, dried and used as anodes in the developed AAO fabrication set-up. The nanoporous AAO structures were fabricated by a simple two step

hard anodization method where a lead sheet was used as cathode. The anodization process was carried out at 140 V applied voltage at $\sim 5^\circ\text{C}$. $0.3\text{M H}_2\text{C}_2\text{O}_4$ was used as the electrolyte.

It has been established that the morphology of nanoporous AAO is affected by various parameters like the anodization time, anodization voltage, nature and concentration of the electrolyte, and the temperature of the electrolytic bath. In this work, two different samples namely S1 and S2 were synthesized by varying the anodization time [Table 1]. The morphology of the as prepared AAO structures was observed with a ZEISS Sigma 300 field emission scanning electron microscope (FESEM).

Table 1. The different anodization parameters for the fabrication of nanoporous AAO.

Sample code	Electrolyte concentration	Electrolyte temperature ($^\circ\text{C}$)	Applied Voltage (V)	Anodization time (min)
S1	0.3M	< 5	140	2
S2	0.3M	< 5	140	4

The sensing ability of the as-fabricated nanoporous AAO structures was investigated by fabricating a parallel-plate capacitor by sputtering a thin gold layer ($\sim 50\text{ nm}$) over the AAO structures, with the non-anodized aluminum component at the base functioning as the other electrode. A gold layer with nanotextured topography was formed as a result of direct deposition of gold over the nanoporous AAO. The dielectric layer (nanoporous AAO) relies heavily on this top electrode for the adsorption of heavy metal ions [5]. Five different concentrations of arsenic ions (0.01, 0.05, 0.1, 0.15, and 0.2 ppm) were used for calibrating the sensors. Capacitive response variations due to changes in As ion concentration were recorded by connecting the as-prepared AAO sensors to a LCR meter. Figure 1 shows a schematic of the experimental sequence. The SEM micrographs of the samples S1 and S2 are shown in Figure 2 and 3.

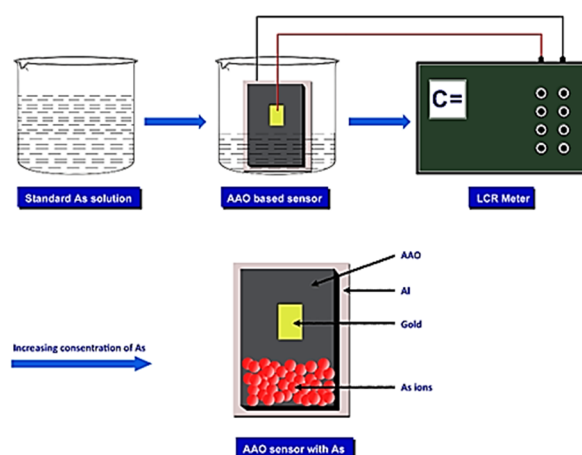


Figure 1. Diagrammatic depiction of the setup for As ion sensing using the as prepared AAO based capacitive type sensor

3. RESULTS AND DISCUSSION

3.1. AAO fabrication and topographical features analysis

Figure 2 (a) and (b) are the SEM micrographs of the top view of the samples S1 and S2, while Figure 3 (a) and (b) are cross sectional SEM micrographs for the samples S1 and S2 respectively. From the SEM micrographs (Top view) of the samples S1 and S2 (Fig 2(a-b)), the extended-range ordering, uniformity, shape and the size of the pores can be observed. From these micrographs, various information regarding the structural morphology like pore diameter, interpore distance, porosity etc. is possible to find out. The diameter of the pores is dependent on the nature of the electrolyte, anodization time and anodization voltage. Here, same electrolyte and anodization voltage has been applied to fabricate the two samples by varying the anodization time. As there is slight difference in the anodization times, therefore variations in the pore diameters for the two samples remain insignificant. A noticeable change in the thickness of the two samples can be observed, which will affect the capacitance of the AAO based capacitor.

The porosity P of the hexagonal cell nanoporous AAO with a pore inside each hexagon can be expressed as follows (where each pore is assumed as a perfect circle) [5]

$$P = \frac{\text{pore area}}{\text{hexagon area}} = \frac{\pi}{2\sqrt{3}} \left(\frac{D_p}{D_i}\right)^2, \quad (1)$$

where, D_p and D_i are the diameter of the pores and the interpore distance of the nanoporous AAO respectively, as shown in Figure 2 (a), (b). The pores density, 'n' of the porous AAO with a hexagonal distribution of pores can be described as the overall quantity of pores present in the 1 cm^2 surface area of the porous AAO, and expressed as follows [19]

$$n = \frac{10^{14}}{A_{hex}} = \frac{2 \times 10^{14}}{\sqrt{3} D_i^2}, \quad (2)$$

where A_{hex} is the surface area of a single hexagonal cell (in nm^2). These structural parameters for the as prepared samples S2 and S4 are analyzed through ImageJ software from the SEM micrographs and calculated using equations (1) and (2), which are shown in Table 2.

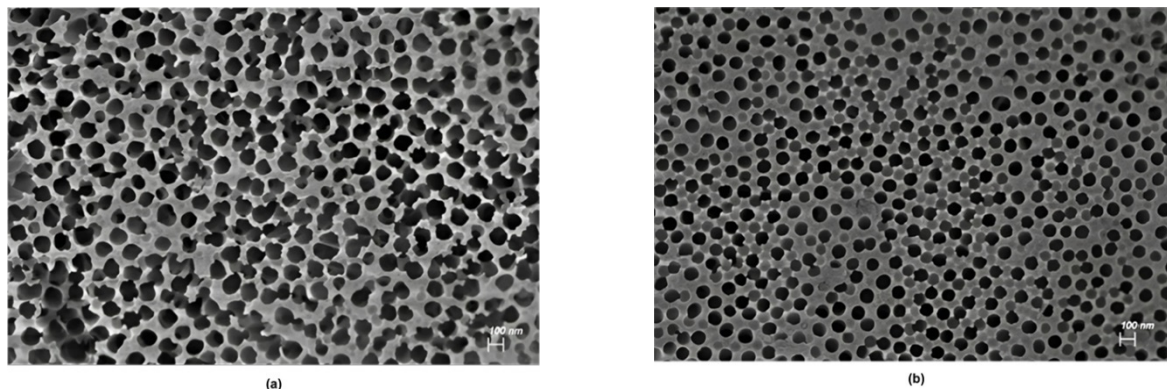


Figure 2. (a-b) SEM micrographs (Top view) of the samples S1 and S2 respectively

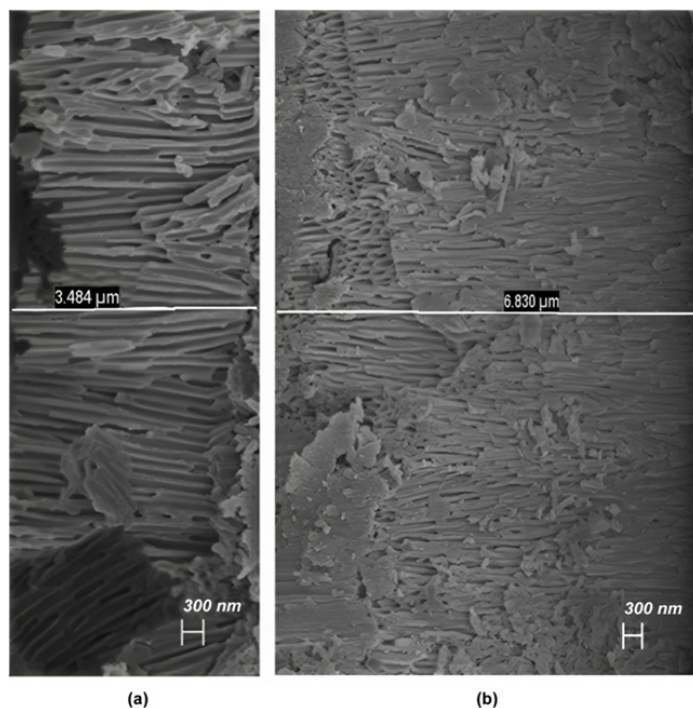


Figure 3. (a-b) Cross-sectional SEM images of the samples S1 and S2 respectively

Table 2. Different structural parameters for the as prepared samples S1 and S2

Sample code	Pore Diameter, D_p (nm)	Interpore Distance, D_i (nm)	Porosity, P (%)	Pore Density, n (Pore/ cm^2)
S1	116	50	4.89	4.6×10^{10}
S2	93	55	2.59	3.82×10^{10}

3.2 Heavy metal ion sensing performance of AAO based sensors

The capacitive response of the as prepared sensors, where the porous AAO layer behaves as a dielectric layer, has been studied with different concentrations of As ions. An increase of the capacitance value was observed with the increase of As concentration for the sensors (Figure 4, 5). This rise in the capacitors' capacitance value can be linked to a modification in their dielectric constant. The permittivity (ϵ) of a dielectric material is directly proportional to its dielectric constant (k). The relationship can be expressed as $\epsilon = k \epsilon_0$. Substituting this relationship into the capacitance equation, the equation becomes

$$C = \frac{k\epsilon_0 A}{d} \tag{3}$$

The incorporation of metal ions with dielectric material can modify its dielectric constant. Metal ions may introduce additional charge carriers, which can increase the dielectric constant of the material. Further, metal ions are generally

associated with increased conductivity, therefore, incorporating a dielectric material with metal ions can enhance its electrical conductivity, which can lead to increased leakage current across the capacitor, reducing its overall effectiveness and potentially affecting the charge retention capabilities. The capacitance of the as fabricated sensor S1 is more than that of the sensor S2 which is shown in Figure 4 and Figure 5.

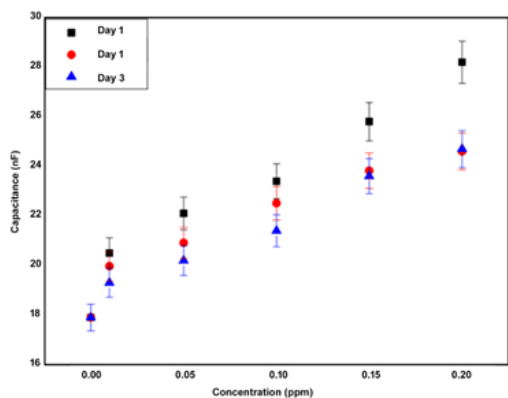


Figure 4. Evolution of capacitance for the sensor S1 as a function of concentration of As ion with 3% error bar

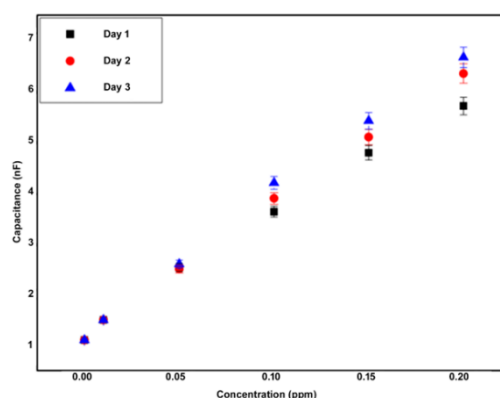
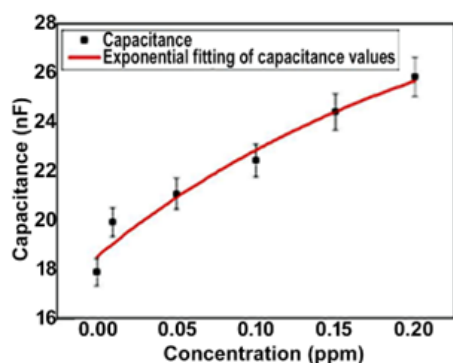


Figure 5. Evolution of capacitance for the sensor S2 as a function of concentration of As ion with 3% error bar

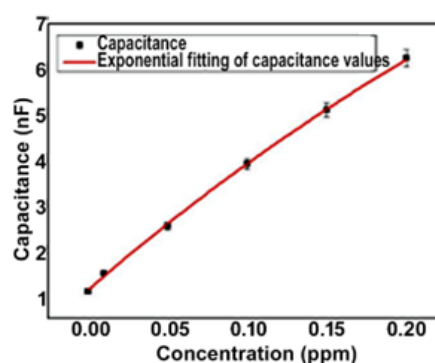
This higher value of the capacitance for the sensor S1 can be attributed to the thickness of the dielectric layer which is thinner than that of sensor S2. But as, the capacitance of a capacitor is inversely proportional to the thickness of the dielectric layer (equation 3), so, the capacitance of S1 is higher than that of S2.



$$y = A1 \cdot \exp(x/t1) + y0$$

$y0 = 30.87956$
 $A1 = -12.35818$
 $t1 = -0.23144$

(a)



$$y = A1 \cdot \exp(x/t1) + y0$$

$y0 = 16.92725$
 $A1 = -15.7992$
 $t1 = -0.51576$

(b)

Figure 6. (a-b) Exponential fitting of concentration Vs capacitance curve for the samples S1 and S2 respectively with 3% error bar

The exponential fitting of concentration versus capacitance curve is obtained through Origin pro 8 software for the as prepared samples S1 and S2 respectively (Figure 6). The working of the as prepared capacitive type sensors is schematically shown in the Figure 7.

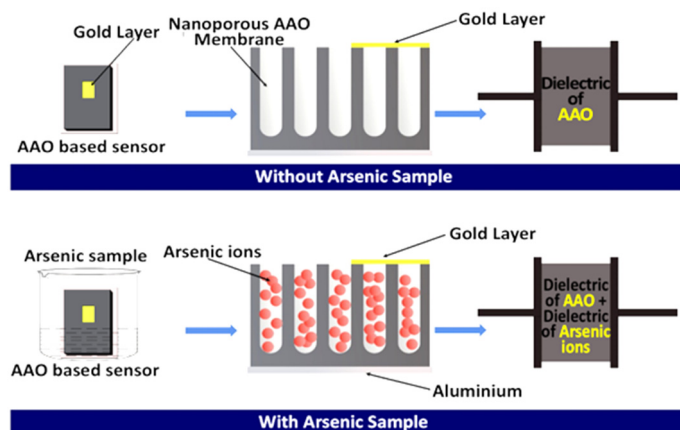


Figure 7. Diagrammatic depiction of the working of the capacitive type sensor with the change in the concentration of the As ions

In order to observe the elemental composition of the as prepared S1 sensor after dipping in the As ion solution, EDS (Energy dispersive X-ray spectroscopy) mapping was carried out in a SEM (Figure 8). The presence of very less amount of As ion (1.35 weight%) has been confirmed through the mapping, as the concentration of As ion solution used in the experiment is very low (0.01 – 0.2 ppm). We have chosen this range of concentrations of As ion as the permissible limit of As in drinking water is up to 0.2 ppm.

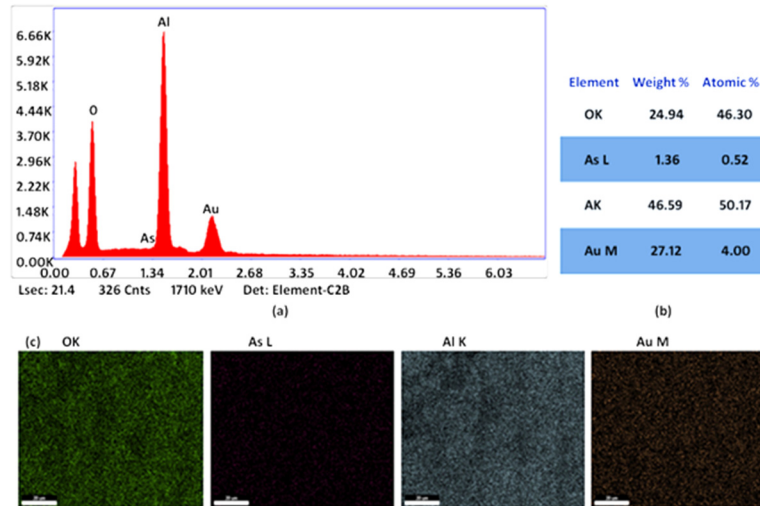


Figure 8. (a-b) EDX pattern of the as developed capacitive sensor S1 after incorporation of As ions (c) EDX mapping of the S1 sensor showing the distribution of O, As, Al and Au atoms

4. CONCLUSIONS

This work reports the successful development of a nanoporous AAO based capacitive type sensor fabricated by a two-step anodization process. Two samples of AAO were prepared by varying the anodization time. Since the anodization time difference maintained here is not high, therefore, a slight change in various parameters like pore diameter, porosity and pore density is observed here. Also, a change in the thickness of the two samples was noticed here. Using these two samples as the dielectric material, two parallel plate capacitive type sensors named S1(2 mins anodization) and S2(4 mins anodization) were prepared, where Aluminum was used as base electrode and Gold as top electrode. To study the sensing behavior of these sensors, an experiment was performed to detect the Arsenic (heavy metal ion) ion. A rise in the capacitance value was observed while the concentrations (in ppm) of the As ion solutions was increased. The mechanism responsible for this performance is directly related to the change in the dielectric constant of the dielectric material (i.e., porous AAO). Incorporation of metal ions into a dielectric material can change the dielectric constant of that material, which directly influences the capacitance of a capacitor. The EDS mapping carried out in a FESEM of the S2 sensor dipped in As ion solutions confirms the presence of As ions.

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РОЗРОБКА НАНОПОРИСТИХ СЕНСОРОВ ЄМНІСНОГО ТИПУ НА ОСНОВІ ААО ДЛЯ АНАЛІЗУ НАЯВНОСТІ ІОНІВ ВАЖКИХ МЕТАЛІВ (МИШ'ЯКУ)

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У цій роботі повідомляється про еволюцію датчика ємнісного типу на основі нанопористого анодного оксиду алюмінію (ААО), виготовленого за допомогою двоетапного процесу анодування з використанням недорогої індивідуальної установки, розробленої власними силами. Конденсатори з паралельними пластинами були виготовлені з використанням алюмінію (Al) як базового електрода та золота як верхнього електрода, де пористий ААО використовувався як діелектричний матеріал. Це продемонструвало чітку залежність значень ємності підготовлених різних сенсорів від товщини діелектричного матеріалу. Розроблені датчики були протестовані на виявлення іонів миш'яку (As). При збільшенні концентрації іона As у водних розчинах спостерігалось збільшення ємності. Наявність іонів As було підтверджено за допомогою картографування EDS (енергодисперсійна рентгенівська спектроскопія), виконаного в FESEM. Цю зміну ємності можна пояснити зміною діелектричної проникності активного матеріалу з включенням іонів металу.

Ключові слова: датчик ємнісного типу; нанопористий анодний оксид алюмінію (ААО); анодування; енергодисперсійна рентгенівська спектроскопія (EDS)