Sensors and Actuators B 210 (2015) 69–74

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

# Effect of oxalic acid concentration on the magnetically enhanced capacitance and resistance of AAO humidity sensor

C.K. Chung*, O.K. Khor, C.J. Syu, S.W. Chen

*Department of Mechanical Engineering and Center for Micro/Nano Science and Technology, National Cheng Kung University, Tainan 701, Taiwan, ROC*

ARTICLE INFO

*Article history:*
Received 23 October 2014
Received in revised form
12 December 2014
Accepted 22 December 2014
Available online 30 December 2014

*Keywords:*
Anodic aluminum oxide
AAO
Humidity sensor
Capacitance
Resistance
Magnetism

ABSTRACT

The enhanced capacitance and resistance behavior of anodic aluminum oxide (AAO) humidity sensor by both the high concentration of oxalic acid and applied magnetism has been investigated. At low relative humidity (RH, ≤45%), the enhanced capacitance response from high concentration of oxalic acid was attributed to phonon-assisted electron tunneling mechanism that was promoted by more acid anions within the AAO pore wall and barrier layer. The other enhancement from magnetic addition was due to the magnetic field induced more orderly arrangement of water molecules for higher capacitance. At high RH (>45%), the capacitance of AAO sensors at different acid concentrations (0.3–0.7 M) with magnetic field was larger than that without magnetic field under the same mechanisms at low RH. Moreover, the medium-concentration AAO sensor exhibited the highest capacitance at RH over 60% due to the enhanced sensing surface area and pore conductance. The short and reliable capacitance response/recovery time was also obtained from the high-concentration AAO sensor under presence or absence of a magnetic field. In addition, the applied magnetism can significantly enhance the ordinary magnetoresistance response of humidity sensors at different acid concentrations at low-to-high RH for more linear-like relationship between the resistance and RH.

## 1. Introduction

The humidity sensors have been used for many applications to the industrial, agricultural and environmental monitoring together with food quality control. The types of humidity sensors include the resistive, capacitive, mass-sensitive and electric magnetic ones [1–3]. Both the capacitive and resistive types attract more attentions because of the easy and low-cost fabrication as well as the fast and reliable response compared to the others [4]. The polymer and ceramic materials were used for most humidity sensors due to their low cost and/or good performance [5–7]. The porous anodic aluminum oxide (AAO) is an electrochemically formed oxide material with high density of nanostructured pores and huge surface area for absorbing water vapor. Therefore, it is advantageous for the humidity sensors in terms of capacitive and resistive detection. In addition, AAO sensors merit high corrosion resistance, good thermal stability and excellent mechanical strength. The surface absorption mechanism and sensitivity characteristics of the AAO humidity sensors have been investigated in many researches. Regarding the capacitive and resistive sensing mechanisms, Khanna and Nahar [1] reported that water molecules were initially chemisorbed on the metal oxide and two hydroxyl groups were formed per water molecule. Then the following water molecules were physically bound with this hydroxyl groups by hydrogen bonds to form the first physisorbed layer. Therefore, the AAO humidity sensor formed at the low oxalic acid concentration (0.3 M) showed that the capacitance increased slowly with rising relative humidity (RH) up to 40–50% and then with a sharp increase at high RH (>50%) [1,8–10]. The sensitivity of the resistive sensor formed by oxalic acid also has a similar response to the capacitance one with a non-linear response. This above sensors suffered from insufficient response over a wide humidity range under low RH (≤45%). Therefore, some studies were reported to promote sensitivity by decreasing the thickness of AAO film [8], increasing the current density [11] or using $H_2SO_4$ solution instead of oxalic acid [1]. The sensors generally had an approximately linear log-normal relationship between the capacitance and RH. However, the log-normal relationship prevents the measured humidity from a high accuracy. Kashi et al. [12] showed that increasing phosphoric acid concentration from 0.2 to 1.0 M could improve the response of sensor. However, the response is still too low at low RH condition.

Thompson [13] showed that the AAO films formed in various electrolytic acids would lead to different distribution of the acid anions within the pore wall and barrier layer. The amount of acid

---

* Corresponding author. Tel.: +886 6 2757575x62111; fax: +886 6 2352973.
*E-mail address:* ckchung@mail.ncku.edu.tw (C.K. Chung).

http://dx.doi.org/10.1016/j.snb.2014.12.096

anions remained in the AAO from high to low in terms of electrolyte was sulfuric acid, oxalic acid, phosphoric acid, and chromic acid. Khanna and Nahar [1] also suggested a phonon-assisted electron tunneling mechanism under low RH in which electron tunneling occurred from one chemisorbed molecule hopping to neighboring anions and could be enhanced by surface anions of the alumina sensors. Therefore the capacitance and surface conductivity of the humidity sensor at low RH would be enhanced at high concentration acid. Moreover, Ibrahim [14] and Pang et al. [15] showed that water molecules under a magnetic field preferentially formed water clusters in which the dipole moments of the water molecules had more orderly arrangement than those without magnetic field. Chen el al. [16] also showed that the magnetic field could promote the bonding of first physisorbed water molecules with chemisorbed molecules to increase their contribution to the dielectric constant and capacitance. The sensitivity of capacitance not only increased at low RH but also at high RH due to the water molecules with more orderly arrangement on the surface of AAO. Additionally, the applied magnetic field can deflect the current path to increase the resistance. Thus, it is of interest to study how the concentration of electrolyte together with the magnetic field can enhance the performance of AAO sensor at low-to-high RH. In this article, we use various concentrations of oxalic acid and the magnetic field to improve the capacitive and resistive responses of the AAO humidity sensors. The high concentration of anions could increase the capacitance of sensor due to the phonon-assisted electron tunneling effect through the increased acid anions in the AAO wall and the sensing surface area. The magnetic field induces orderly arrangement of water molecules and magnetoresistance effect to enhance both capacitance and resistance sensitivity at low-to-high RH. In addition, the short and reliable response/recovery time was also obtained in the proposed sensor device.

## 2. Experimental details

### 2.1. Fabrication of AAO humidity sensor

A pure aluminum foil (99.99%, Alfa Aesar, USA) with 0.25 mm thickness was electropolished in a mixture of perchloric acid and ethanol ($HClO_4$:$C_2H_5OH$ = 1:2, v/v) at 0 °C for 20 min to polish the Al surface. Then it was placed in a proprietary holder (diameter = 1.5 cm) with an exposed area of 1.76 $cm^2$. The first anodization process was performed by means of the three-electrode electrochemical cell and the potentiostat (Jiehan 5000, Taiwan) under 2-step direct current anodization at 40 V and three concentrations of 0.3, 0.5 and 0.7 M oxalic acid solutions for 1 h, respectively. The three-electrode electrochemical cell consists of the platinum mesh as the counter electrode, the aluminum foil as the working electrode, and the saturated calomel electrode (SCE) as the reference electrode. The relatively high temperature of 25 °C was controlled by an isothermal bath to increase growth rate of AAO. After the first step of anodization, the specimens were immersed in a mixture of 5 wt% $H_3PO_4$ and 1.8 wt% $H_2CrO_4$ at 55 °C for 4 h to remove the pre-textured $Al_2O_3$ on Al surface as a self-assembled mask. Then the second step of anodization process was resumed to form the new AAO layer under the same conditions as the first anodization.

The morphology and thickness of AAO films were examined by Ultra-High Resolution Field Emission Scanning Electron Microscope (UHRFE-SEM, AURIGA Zeiss, Germany) operated at 15 kV. The gray-scale imaging analysis technique was used to estimate the mean value of pore size distribution by using the commercial software (ImageJ). In addition, photoluminescence (PL) spectra of the various concentrations of AAO templates were used for examining anions evolution by a micro-PL (Labram HR, Jobin Yvon, France) with a 325 nm Helium-Cadmium laser as an excitation light source.

### 2.2. Experimental setup

A Pt thin film was deposited on the surface of AAO sensor as one electrode using sputtering process at 20 mA for 180 s in the Auto Fine Coater (JFC-1600, JEOL, Japan). The thickness of Pt film was about 10 nm and did not cover the AAO pores to provide access of any ambient air to the intermediated aluminum oxide layer. The sensor was placed into a proprietary measurement system to investigate the variation of the capacitance and resistance from low to high RH levels under presence and absence of the applied magnetic field of 0.058 Tesla (T). The system was combined by two chamber, a computer, LCR meter and commercial humidity sensor and it was reported in our previous work [16]. The first chamber was accessed the flows of dry air and wet air to adjust the relative humidity, then the controllable and stable humidity level (15–80%) was achieved in second chamber and measured with a commercial sensor (Lascar, EL-USB-@-LCD, UK). The capacitance and resistance of AAO humidity sensor were measured via a LCR meter (HIOKI 3522-50, Japan) in 1 kHz and 100 kHz, respectively. The experiment temperature was maintained at ambient temperature (about 25 °C). The sensors were placed at the steady humidity level for 5 min before recording the values of capacitance and resistance. The sensor was repeatedly measured 3 times to obtain average value at various RH conditions. Regarding the response/recovery behavior, the AAO humidity sensor was measured at RH 15% for 2 min and then rapidly increasing to RH 50% for 2 min and repeated it for 3 times. The resistance response ($S_R$) to humidity change of the sensor was calculated as follows:

$$S_R = \frac{\Delta R}{R_{15}} \tag{1}$$

where $R_{15}$ is the resistance of the sensor at minimum RH = 15% and $\Delta R$ is the absolute value of change of resistance induced by the increase of RH relative to 15% RH. It is noted that evolution of capacitance response ($S_c$) to humidity change of the sensor is similar to the capacitance variation which has been defined and discussed in Ref. [16], therefore we only discuss the trend of evolution of capacitance and that for the resistance together with its resistance response to humidity change.

## 3. Result and discussion

Fig. 1(a)–(c) shows the SEM plane-view micrographs of the AAO films formed by 2-step anodization at 40 V at 25 °C for 1 h in oxalic acid solution at concentrations of 0.3, 0.5 and 0.7 M, respectively. The mean pore diameters of AAO analyzed by Image J software are 55.1 nm (0.3 M), 55.9 nm (0.5 M) and 56.8 nm (0.7 M), respectively, with an error of 0.8 nm each sample. It slightly increases with increasing acid concentration. It is because the increased oxalic concentration raises the anodizing current for increasing local temperature and higher dissolution rate for a little larger pore diameter. Fig. 1(d)–(f) shows the SEM cross-sectional micrographs of the corresponding AAO films in Fig. 1(a)–(c) for thickness examination at 0.3, 0.5 and 0.7 M. The thicknesses of AAO are 16.0 μm (0.3 M), 19.1 μm (0.5 M) and 22.3 μm (0.7 M), respectively. The thickness or growth rate of AAO film increases with increasing electrolyte concentration due to general chemical reaction proportional to reactant concentration.

Fig. 2 shows the relationship between the capacitance and relative humidity of the AAO humidity sensors at various oxalic acid concentrations under without (solid symbol) and with (empty symbol) magnetic field strength of 0.058 T. In the case of no magnetic field, the capacitance of AAO film at 0.3 M has a value of 0.65 nF at the lowest RH of 15%. When the RH increases to 45%, the capacitance slightly increases to 4.06 nF. For the condition of RH over 45%, the capacitance obviously increases. Taking 80% RH for example,