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NANO-POROUS ALUMINA HUMIDITY SENSORS

In this paper the details of porous alumina humidity sensors fabricated using anodic aluminium oxidation are presented. The main aim of this study is to establish relations between technological process parameters and electrical properties of sensors. Surface morphology was investigated by scanning electron microscopy. Impedance spectroscopy was used to identify electrical parameters of the sensor.

Keywords: ceramic humidity sensors, alumina film, impedance spectroscopy

1. INTRODUCTION

Humidity, besides temperature, is one of the most frequently measured physical quantities. Whereas the measurement of temperature can nowadays be done with a satisfactory accuracy, measurement of the water vapour content in air appears to be much more complex. Humidity sensing has attracted considerable attention over many years due to its great importance in numerous applications ranging from domestic to industrial [1, 2]. In order to satisfy the numerous application requirements a wide variety of humidity sensing devices become available.

The most common humidity sensors are based on moisture absorbing polymers [3-5]. Humidity sensors based on polymers are very attractive due to their low cost and excellent performance. Polymer sensors, however, usually suffer from low resistance to liquid water and poor mechanical properties.

Sensors based on ceramic materials seem to overcome those problems. Ceramic sensors have shown advantages in terms of their mechanical strength, their resistance to chemical attack and their thermal and physical stability [6]. Among ceramic materials alumina is frequently used.

A porous layer of aluminium oxide has been used for many years for fabrication of humidity sensors [7]. Such sensors have relatively good properties. They are stable, fast, have small hysteresis, a low temperature coefficient, they do not require

any service, they work in a wide range of temperatures, pressures and humidities. However, limitations in microscopy and in measuring equipment restricted the ability to fully evaluate the properties of alumina-based humidity sensors. Recently, progress in experimentation techniques caused that nano-porous alumina again has drawn a significant attention of many research groups [8-10]. Additionally, nano-porous alumina is a potential material for templates and masks suitable for the fabrication of nanosized structures [11, 12].

It is widely established that the porosity and morphology of an Al_2O_3 layer is responsible for unique properties of alumina based sensors [13-17]. Water molecules are absorbed in the sensor‘s porous structure resulting in changes of their electrical properties. The control of pore structure, such as pore diameter, pore diameter distribution, thickness of porous layer, etc., has crucial significance for the sensitivity and selectivity of sensor. Those parameters depend mainly on conditions of the anodizing process.

Our earlier studies on alumina-based humidity sensors had been of a preliminary nature [18-20]. Usually, the electrical capacitance at a single frequency was used as a measure of sensor‘s response. It was unclear why the sensors prepared in similar manner had sometimes dramatically different electrical properties. The application of impedance spectroscopy allowed better understanding of sensor properties. However, due to lack of a proper representative group of sensors those studies remained unfinished.

In this work we present the results of a representative group of nanostructured porous alumina humidity sensors. The fabrication process parameters were carefully selected, so their influence on sensors performance and porous layer structure can be investigated. The main aim of this study is to establish a relationship between fabrication process parameters and electrical properties of sensors.

2. EXPERIMENTAL

2.1. Influence of number of wires reduction

The main reactions involved in the anodizing process are listed below. Reaction (1) corresponds to the whole electrochemical process with oxide growth at the anode and hydrogen evolution at the cathode. At the anode partial alumina dissolution occurs (2) leading ultimately to the formation of porous alumina.

$$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2, \tag{1}$$

$$Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O. \tag{2}$$

2.2. Sensor fabrication

The quality of an electrochemical process is largely dependant on metal surface proper pre-treatment and surface condition [12, 21]. High purity (99.999%) aluminium foil 0.5 mm thick was used for the fabrication of sensors. Plates with a dimension of 30 × 30 mm were cut. Each plate was then separately cleaned. Firstly, in order to remove surface irregularity and scratches, the aluminium plates were mechanically cleaned. Afterwards, to remove the remaining grease and oxide layer, the plates were chemically cleaned. For this purpose solutions of NaOH and H_2SO_4, H_3PO_4, HNO3 were used. This process was repeated several times.

Once the surface was prepared, the anodic film was built. The plates were anodized in 2.5% and 10% aqueous solution of sulphuric acid. The Hameg HM 8142 power supply working in the current-control mode was used. An electric current was measured with the Metex M-4640A working in the ammeter mode. An anodizing aluminium plate was used as the anode, while a lead plate was used as the cathode. Different current densities, ranging from 2.5 to 80 mA/cm^2, and different times of electrolysis processes, ranging from 30 to 240 minutes, were used to form the dielectric layer.

On one side of the anodized surface a gold electrode about 220 nm thick and 10 mm in diameter was sputtered. The other electrode was aluminium foil, which was accessed by physical removal of its surface oxide layer. Wires were connected to the electrodes using conducting silver glue.

2.3. Measurements

Measurements of sensor parameters at different values of relative humidity were carried out using hygrostatic solutions. Selected 9 saturated aqueous solutions with appropriate salts were used. The air relative humidity (RH) over those solutions was 11%, 20%, 33%, 42%, 54%, 66%, 76%, 86% and 97% respectively. The measurements took place at a controlled temperature of 25°C.

Measurements of sensor impedance spectra were performed in the frequency range from 0.1 Hz to 1 MHz with an amplitude of 50 mV using the impedance analyzer Solartron 1260. A PC computer with Z60/ZView software (Scribner Associates Inc.) provided control over the whole system and allowed measured data acquisition and analysis.

Investigation of sensors surface morphology has been performed using field emission scanning electron microscopes (SEM) Hitachi S-4700.

3. RESULTS AND DISCUSSION

The surface morphology of the sensors fabricated at different anodization times was investigated using SEM and is presented in Fig. 1. The evolution process of the

sensor surface is clearly visible. After 30 minutes of anodization at 10 mA the surface of the sensor is covered with nanopores of 5-10 nm in diameter (see Fig. 1a). After 120 minutes of anodization the diameters of nanopores increase up to 15-20 nm (see Fig. 1b). The pores are evenly distributed and cover the whole sensor surface. After longer anodization times the nanopores disappear from the surfaces and a porous nanocrystalline-like structure is formed (see Fig. 1c).

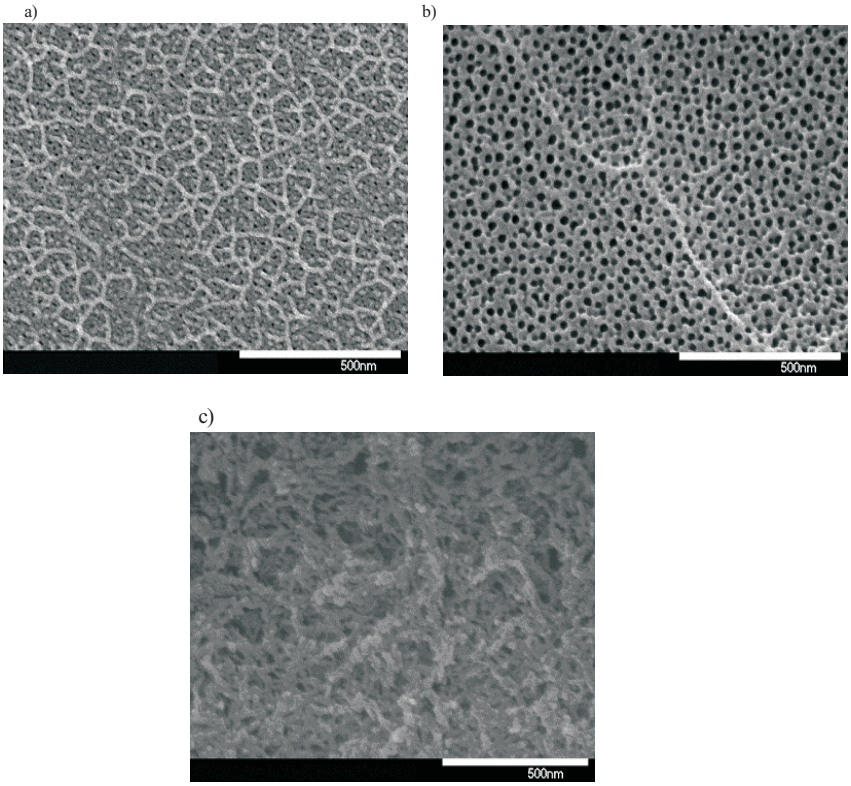

Fig. 1. SEM images of sensors surfaces: 2.5% of H_2SO_4, 10 mA/cm^2, 30 min (a), 120 min (b) and 240 min (c).

Impedance spectroscopy was used to investigate the electrical properties of fabricated humidity sensors. The impedance spectra of two sensors fabricated at different anodizing process times (30 and 240 minutes) are presented in Fig. 2. A module of impedance was chosen as indication of sensor response. In every case, with an increase of humidity the impedance module decreases. However, the shapes of these plots differ significantly between each other. The sensor prepared with longer anodizing time has the best sensitivity to water in the frequency range of 100 Hz ÷ 3 kHz, while the other one between 2 Hz ÷ 20 Hz. At suggested frequencies the first sensor has a one-

-order-of-magnitude lower modulus of impedance than the second one. The sensors' sensitivity, which is defined as depicted by Eq. (3), is different as well. In case of the sensor with longer anodizing time the sensitivity is higher (S = 1.62) than for the other one (S = 1.23). It can be concluded that anodizing process parameters have an enormous influence on the electrical properties of alumina humidity sensors.

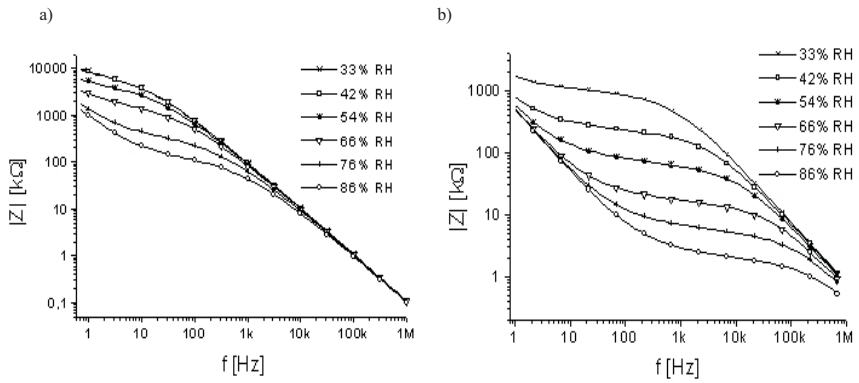

Fig. 2. Bode plots of the sensor at different relative humidity. Anodization process: 2.5% H_2SO_4, 2.5 mA/cm^2, 30 minutes (a) and 240 minutes (b).

It is often convenient to describe sensors' behaviour using resistance, capacitance or modulus of impedance at a single frequency [22-23]. The frequency of 1 kHz is usually chosen for this purpose. It allows easy comparison of obtained relations with other research groups, especially for those who use RLC bridges for electrical measurements. This approach, however, can lead to false conclusions. As it has been shown above the sensors can have different frequency ranges of the highest sensitivity. The choice of frequency can have a great influence on the obtained results and consequently on drawn conclusions. Therefore, in this paper for each sensor the measurement frequency was selected individually. Namely, based on Bode plots taken for each sensor, from the frequency range of the highest sensitivity the middle frequency was selected.

In Figures 3 and 4 the modulus of impedance as a function of relative humidity for different anodization times and currents is shown, respectively. It can be seen that increasing anodizing time and current have similar impact on sensors' behaviour. Sensor impedance tends to decrease. Simultaneously, sensor sensitivity is increased and the linearity of plot (in log-lin scale) is improved. These relations are confirmed by results presented in Fig. 5 and Fig. 6, where the sensitivity of different sensors is compared. In this case sensitivity S is defined as the ratio of impedance at RH of 33% to impedance at RH of 86% for a chosen frequency, what is depicted by Eq. (3):

$$S = \frac{|Z|_{f=const}\,(RH = 33\%)}{|Z|_{f=const}\,(RH = 86\%)} \quad . \tag{3}$$

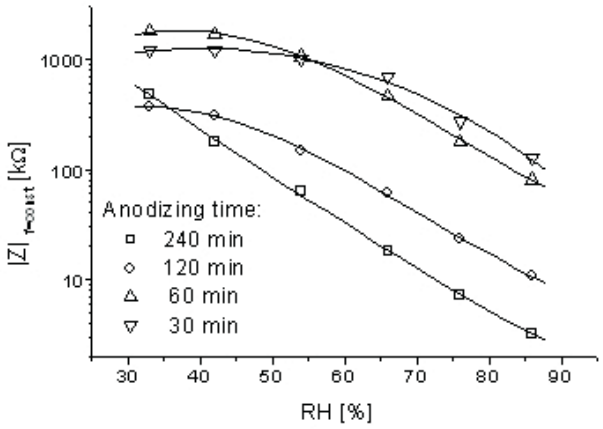

Fig. 3. The influence of anodizing time on sensor performance (2.5% of H_2SO_4, 2.5 mA/cm^2).

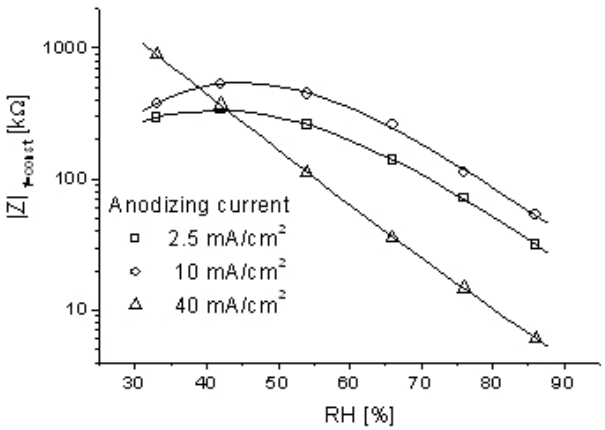

Fig. 4. The influence of anodizing current on sensor performance (2.5% of H_2SO_4, 60 min).

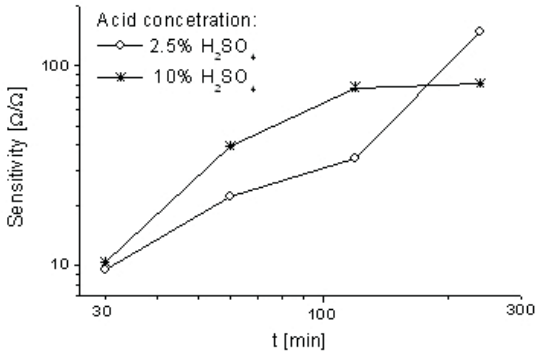

Fig. 5. The influence of anodizing time and acid concentration on sensor sensitivity (2.5 mA/cm^2).

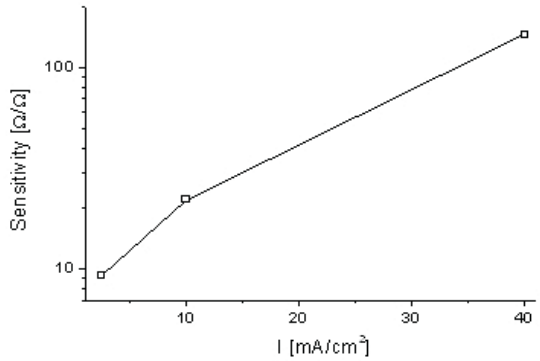

Fig. 6. The influence of anodizing current on sensor sensitivity (2.5% of H_2SO_4, 60 min).

It was found that acid concentration in the anodizing solution only slightly influences sensor performance. For short anodizing times, high acid concentration improves the sensitivity. This effect is reversed for long anodizing times.

The dynamic behaviour of the sensor‘s response was investigated as well. Again, sensor fabrication parameters are influencing the sensor performance. The response times of the sensors due to changes of relative humidity from 76% to 33% were investigated and are presented in Fig. 7. In case of the sensor prepared using long anodizing times (240 minutes) the response reaches a stable level after a few minutes (Fig. 7b). In contrast, for the sensor prepared using short anodizing times (30 minutes) the response was so long that even 12 hours of observation were too short to obtain a stable level of response (Fig. 7a).

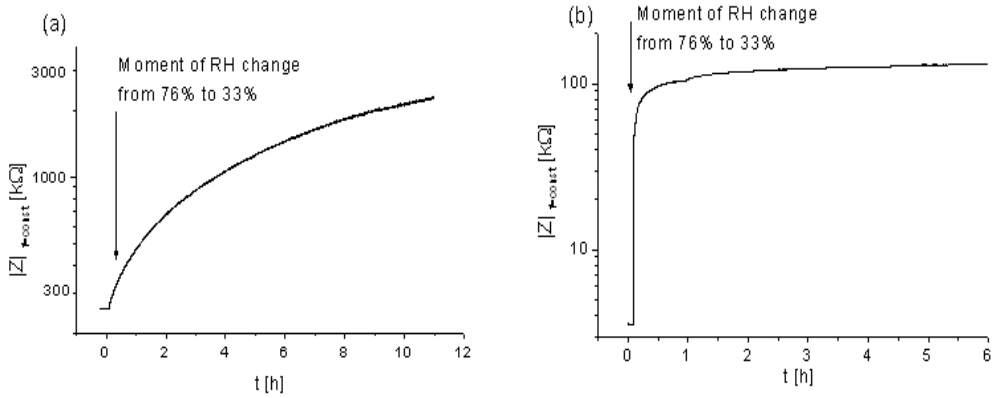

Fig. 7. Response of the sensors to relative humidity change from 76% to 33%. Fabrication parameters: 2.5% of H_2SO_4,10 mA/cm^2, 30 minutes (a) 240 minutes (b).

An influence of sensors fabrication parameters can be also observed in the case of hysteresis measurements (Fig. 8). The measurements were performed after a long equilibrium time in high humidity (more than 12 hours). 30-minute time intervals between measurements were executed. The relative humidity was changed subsequently to 33%, increased to 86% and then decreased back to the starting point of 76%. Due to longer response times of the sensor with shorter anodizing time (30 minutes), the effect of hysteresis was emphasized (Fig. 8a).

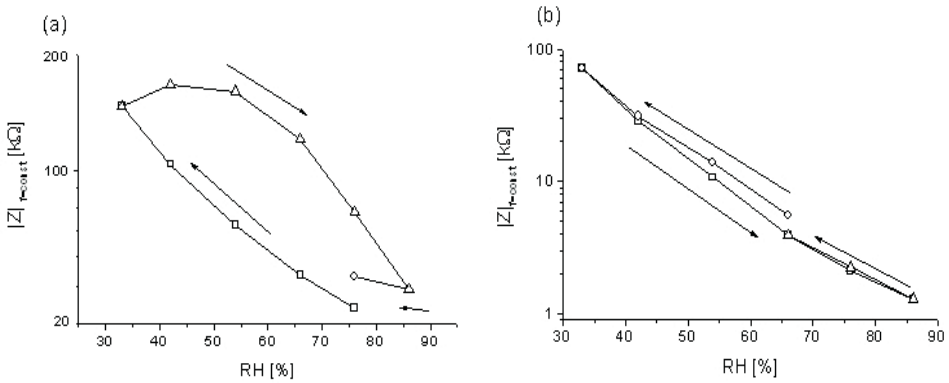

Fig. 8. Hysteresis of the sensor. Arrows indicate the direction of humidity changes. Fabrication parameters: 2.5% of H_2SO_4,10 mA/cm^2, 30 minutes (a) 240 minutes (b).

4. CONCLUSIONS

In this work the results of aluminium oxide humidity sensors investigation have been presented. Parameters of the sensor fabrication process were carefully selected in order to determine their influence on sensor performance and porous layer structure. Scanning electron microscopy proved the nano-porous structure of the sensors. Impedance spectroscopy performed in a wide frequency range was used to identify the electric parameters of the sensor. Long anodizing times (240 minutes at 10 mA/cm^2) enables obtaining sensors with the highest sensitivity. The hysteresis is also lowest for these parameters of sensor fabrication.

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