RELATIVE HUMIDITY SENSORS BASED ON FREE NANOSTRUCTURED AL_2O_3 MEMBRANES WITH OPEN-ENDED PORES

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Abstract – Volumetric-surface variants of vertical direction capacitive MDM (metal-dielectric-metal) structures based on high-ordered matrices of free anodic porous alumina membranes for applications in relative humidity sensing elements were designed. The improved humidity sensitivity (4 pF/%), reduced response time and recovery time over a wide humidity range were obtained due to preparing of 30-70 μm thickness nanostructured alumina membranes with open-ended and widened pores (up to 90 nm) without the barrier layer. A special combined method composed of the smooth slow voltage drop at the final stage of the two-stage anodization with the cathode polarization and with the alumina chemical etching was developed to thin and remove the barrier layer. Such the technological approach allowed us to eliminate the effect of electrolyte anions embedded in pore walls of Al_2O_3 membranes for humidity sensing elements during the adsorption and desorption processes.

I. Introduction

Nanostructured anodic porous alumina can be used as an active humidity sensing element in the humidity sensors [1, 2] because the electrochemical process allows the capillary nanochannels to be formed and their geometrical parameters (diameter and length) to be varied. Anodic porous alumina membranes both with a dense alumina barrier layer at the pore bottoms and without this layer with open-ended pores [3] can be used as starting material to design various humidity sensors. The structural parameters determine sensitivity of nanoporous alumina to the humidity variation. These parameters are controlled by the electrolyte composition and electrical and temperature formation regimes. Conductive electrodes are possible to be formed either on one or both sides of the alumina membranes resulting in the fabrication of vertical or horizontal (interdigitated) capacitive relative humidity (RH) sensing structures.

II. Results and discussion

The test sensing elements designed for the humidity sensors based on nanoporous alumina membranes are the volumetric-surface variants of capacitive MDM (metal-dielectric-metal) structures of the vertical direction (Fig. 1). To improve humidity sensitivity, reduce response time and recovery time of the test sensing elements designed, we use free membranes based on the high-ordered matrices of anodic nanoporous alumina with open-ended pores without the barrier layer.

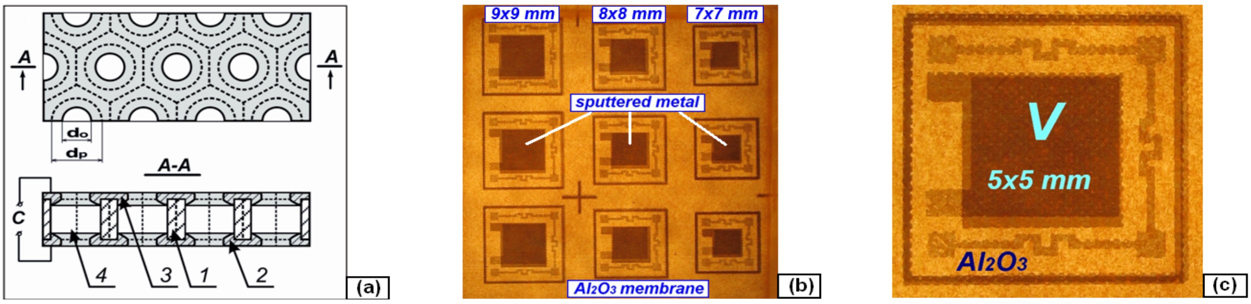

Figure 1 – Design of volumetric-surface capacitive MDM test structures of humidity sensing elements: (a) schematic explanation (d_p is pore diameter; d_o is a pore opening after the metal films sputtering; (1) is a free membrane based on anodic nanoporous alumina without the barrier layer; (2) and (3) are bottom and top permeable conducting plates not occluding pore entrances; (4) are open-ended pores); (b) image of test structures (9×9, 8×8, 7×7 mm) (alumina membrane thickness is 50 μm; pore diameters are 70 nm; V electrodes thickness is 100 nm); (c) image of a single element (V plates size is 5×5 mm)

Such membranes were formed by the two-stage electrochemical anodization in the 5% $H_2C_2O_4$ solution at the potentiostatic regime (45, 50, and 55 V) with the use of the barrier layer thinning method by the slow voltage drop to 5 V at the final anodization stage combined with the cathode polarization either in the 0.5M $H_2C_2O_4$ or in the neutral 0.5M KCl solution at (-4) V for 21, 24, 27, 30, and 35 min for the alumina thicknesses of 30, 40, 50, 60, and 70 µm correspondingly and with the alumina chemical etching in 5% H_3PO_4 for 5-45 min at 25-30 °C. Such the technology allows obtaining high uniformity of pore sizes (50-90 nm) and eliminating the effect of electrolyte anions (O^{2-}, OH^-, and $C_2O_4^{2-}$) embedded in pore walls on the adsorption processes due to the decrease of the embedded anions concentration at the chemical etching.

Humidity permeable counter electrodes from the both sides of membranes formed by the metal (V, Ti, Ta, Mo) films sputtering 50-200 nm in thickness were used as the conducting electrodes of the MDM structures. The metal films thicknesses were shown by the simulation to be not more than 3-4 d_p to provide alumina matrices with open-ended pores.

Fig. 2 shows a dependence of sensing elements capacity on relative humidity (RH) at the RH increase from 10% to 90% and at the reverse RH decrease to the recovery of initial values (Fig. 2 (a)) and also a comparative analysis of the effect of the alumina structure parameters on the humidity sensors capacity at the RH variation (Fig. 2 (b)). Minimum values of the MDM nanostructures capacity are shown to be 22-35 pF at RH ~10% and amount to 370-390 pF at RH ~90%, i.e. the sensitivity of the humidity sensors is more than 4 pF per %. This indicates a high sensitivity index to allow signal digitizing at the electronic signal-conditioning circuit. Moreover, as Fig. 2 (a) shows, hysteresis value does not exceed 20 pF.

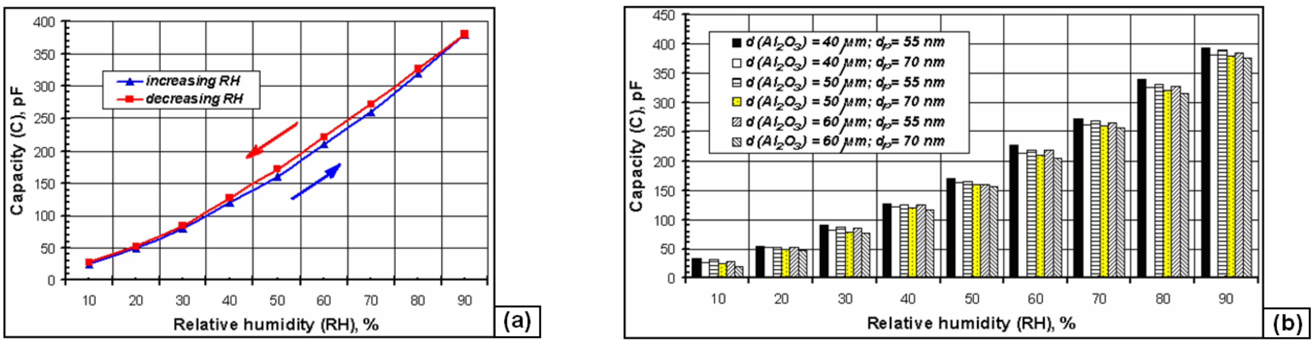

Figure 2 – Dependences of sensing elements capacity on relative humidity: (a) alumina film thickness is 50 µm; pore diameters are 70 nm; (b) a comparative analysis of the effect of the alumina structure parameters on the humidity sensors capacity at the RH variation

Fig. 3 (a) represents the comparative experimental values for the response (t_{res}) and recovery (t_{rec}) time during the adsorption process at the RH increase and the desorption process at the RH decrease for the sensing element (7×7 mm) based on the alumina free membrane 50 µm in thickness and 70 nm in pore diameters. Fig. 3 (b) shows a comparative analysis of kinetic dependences of sensing elements capacity during two cycles for different membranes thicknesses (60, 50, 40 µm). Humidity permeable counter electrodes from the both sides of membranes were formed by the Ti films sputtering 150 nm in thickness and Mo films sputtering 120 nm in thickness correspondingly. Kinetic testing procedures demonstrate that response time values are from 12 to 37 sec and recovery time data are from 3 to 8 sec during the RH increase from 10% to 30, 50, 60, 70, 90% and the RH decrease from 30, 50, 60, 70, 90% to 10% correspondingly (Fig. 3 (a)), and t_{res} are 41, 36, 32 sec and t_{rec} are 11, 9, 7 sec during the RH increase from 10 to 90% and the RH decrease from 90 to 10% for different membranes thicknesses correspondingly (Fig. 3 (b)). Observed recovery time values are much shorter than response time data.

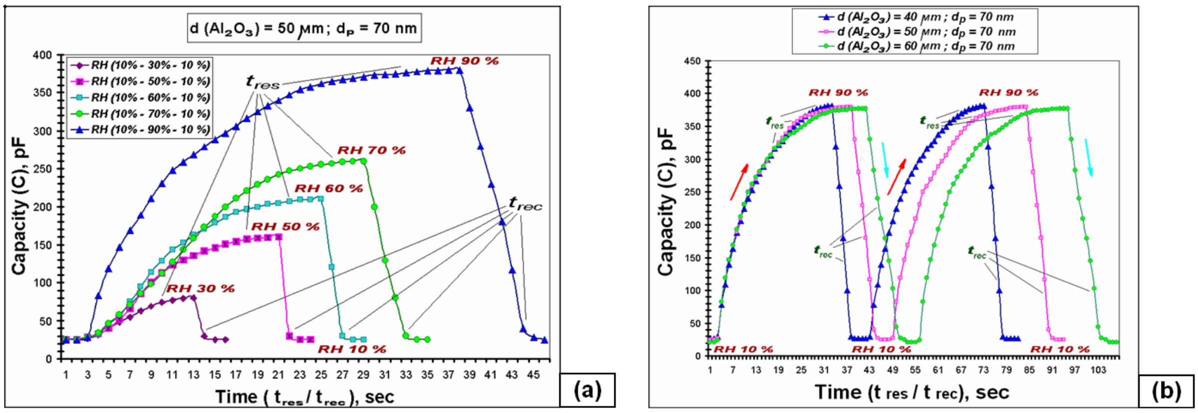

Figure 3 – Kinetic dependences of sensing elements capacity during the adsorption and desorption processes: (a) t_{res} is during the RH increase from 10% to 30, 50, 60, 70, 90%; t_{rec} is during the RH decrease from 30, 50, 60, 70, 90% to 10% (alumina free membrane thickness is 50 µm; pore diameters are 70 nm); (b) t_{res} is during the RH increase (two cycles) from 10 to 90%; t_{rec} is during the RH decrease (two cycles) from 90 to 10% (alumina free membranes thicknesses are 40, 50, 60 µm; pore diameters are 70 nm)

III. CONCLUSION

Thus, the improved humidity sensitivity, reduced response and recovery time over a wide humidity range were obtained due to preparing and using of alumina membranes of thicknesses from 30 to 70 µm without the barrier layer with open-ended and widened pores from 50 to 90 nm in diameters. Such technology allows to eliminate the effect of electrolyte anions (O^{2-}, OH^{-}, and $C_2O_4^{2-}$) embedded in pore walls on the adsorption and desorption processes in humidity sensing elements due to the decrease of the embedded anions concentration at the chemical etching and to improve the performance of humidity sensors.

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