HUMIDITY EFFECT ON CHIP CAPACITORS WITH Al$_2$O$_3$ MULTISTAGE ANODISED FILMS

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In this paper the properties of capacitors with porous-barrier and barrier-type Al$_2$O$_3$ layers under humidity tests are described and compared. The capacitance, conductance and dissipation factor of these structures were measured as a function of relative humidity ranging from 11% RH to 94% RH. It has been found that the dependences of electrical conductance on relative humidity on a log-log scale are linear with the slope from 0.026 to 8.19. For capacitors with the porous-barrier type layer the slopes were below unity in the whole humidity range while for capacitors with the barrier-type layer this was only true in the low humidity range (below 60% RH). The moisture effect on capacitors with solder bump and NiCr electrodes was extremely small. On the other hand the presence of chromium lying direct on Al$_2$O$_3$ film caused a rise in humidity sensitivity. The new ingenious technique of Al$_2$O$_3$ dielectric layer preparation proposed affords the possibilities of producing capacitors with very low sensitivity to moisture in both the low-and high-humidity ranges.

KEY WORDS: Chip capacitors, aluminum oxide capacitors, humidity effects

1. INTRODUCTION

Aluminum oxide films have been studied extensively because of its application to capacitors with barrier-type dielectric layers and to humidity sensors with porous-type layers structures. A physical understanding of Al$_2$O$_3$ humidity sensors has been the subject of numerous investigations[1-9]. New improved configurations of capacitive humidity sensors have also been reported in many papers[10-13]. The barrier layer, which is applicable to capacitors[14-15], has the already weak effect of moisture additionally minimized by sealing. However in some applications sealing is not recommended, for example in microwave circuits[16-17]. In these cases the behaviour of capacitors exposed to a moisture environment needs to be known. It has been found that barrier films are limited in thickness, whereas porous layer have no such limitation but may have inferior dielectric properties especially with regard to poor moisture resistance.

In recent years several attempts at improving the dielectric properties of anodic aluminum films have been reported[18-19]. In our earlier studies combining porous- and barrier-type Al$_2$O$_3$ oxide films and also single Al$_2$O$_3$ barrier-type layer were investigated[20-24]. The Al$_2$O$_3$ barrier layer produced on a porous layer allowed one to extend the range of the capacitance per unit area towards low values. The chip

capacitors with these layers formed on Al-foil were found to be useful in microwave applications. They had a low dissipation factor, high breakdown field strength and satisfactory stability during long-term tests.

The aim of this paper is to describe the properties of these capacitors under long- and short-time humidity tests. The porous-barrier aluminum oxide films are discussed by comparing with the barrier aluminum oxide. For each type of capacitor, various materials for the top electrode were examined.

2. EXPERIMENTAL

Thin film capacitors were prepared on high purity Al-foil of 0.1 mm thick. Dielectric layers were formed by anodization at room temperature. The electrolyte for the porous Al_2O_3 was sulphuric and chromic acid solution, whereas for the barrier layer it was a mixture of ammonium tetraborate and ethylene glycol. The dependences of oxide aluminum film thickness versus the process conditions for both anodisation types have been defined in a previous paper[22]. The film thickness was controlled by anodising under predetermined conditions to obtain the correct values. During the formation of the porous layer the current density was maintained at a constant value of 4.5 mA/cm². The barrier layer was formed first at constant current density of about 0.5 mA/cm² and then at a constant voltage of about 270 V. This procedure gave the porous-barrier film structure with a thickness of about 0.6 μm. The film thickness was measured on a test substrates by the direct observation of sections through anodic films using scanning electron microscope. The single barrier layer formed on bare Al-foil using only the second part of process described above had a thickness of about 0.35 μm. The top electrodes, with an area of 0.45 mm², were made using vacuum deposition and photolithographic processes to form the structures as shown in Fig. 1. The measurement set consisted of two devices: firstly with
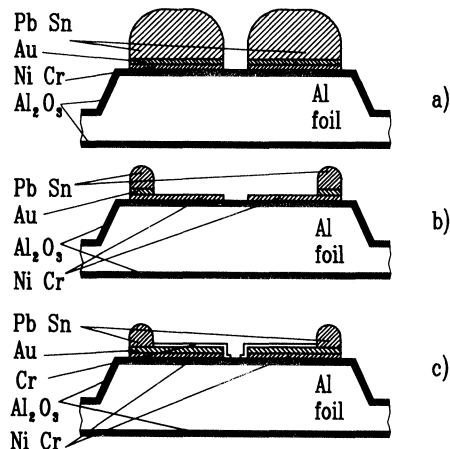

FIGURE 1   Cross sections of various capacitor structures with (a) solder bump contacts on whole surface of top electrode and (b,c) solder bump contacts on part of the top electrodes.

solder bump contacts on the whole surface of the top electrode (Fig. 1a) and secondly with solder bump contacts covering only 1/3 of the top electrode (Fig. 1b–c). The residual parts of the electrode area was covered by a 100 nm NiCr film or by a 100 nm NiCr–100 nm Au–100 nm Cr multilayer. In the second case the Cr final layer extended beyond the normal electrode area. The Cr film lay directly on the Al_2O_3 film over certain areas yielding a 40% increase in electrode area. The solder bump contacts were made by full covering the conductor thin film with solder alloy. The devices with full bump contacts and with partial bump contacts with NiCr–Au–Cr film electrodes or devices with full bump contacts and with partial bump contacts with NiCr film electrodes formed the pairs of tested capacitors which were fabricated in the same technological process. Each measured element consisted of two capacitors in series.

The capacitance, conductance and dissipation factor were measured as a function of relative humidity using a precision semi-automatic bridge type Tesla BM 484 at a frequency of 1.5 kHz. The measured admittance was attained as a parallel combination of capacitance C and conductance G. The characteristics were measured in the range from 11% RH to 94% RH at a temperature of about 23°C employing standard constant humidity solutions[25]. The humidity characteristics were measured by sealing the devices in glass chambers containing salt solutions which maintained a known humidity as determined by known humidity sensors[26]. The measurements were performed after 15 minutes exposure to humidity for a few pairs of capacitors samples.

For the long-time humidity test the capacitors were exposed to 95% RH at the temperature of 40°C for 1344 hours. During this test the capacitance and conductance of the capacitors were periodically measured. The measurements were performed at normal room conditions (in the low humidity range below 60% RH and at a temperature of 20 ± 2°C) after a few hours of storage. The sample size of the tested capacitors was in the range from 147 to 177. The long-time investigations were performed only for single capacitors with bump contacts on the whole electrode area. It means that the capacitance and conductance were measured between the bump electrode (top electrode) and the Al-foil (bottom electrode). The electrode area was 0.22 and 0.45 mm^2.

To separate the reversible from irreversible changes of parameters connected with temperature the measurements of capacitance and conductance versus temperature were performed in the temperature range of 20–100°C. Temperature coefficients of capacitance TCC and of conductance TCG were estimated assuming that these dependences were linear in the temperature range studied—a reasonable approximation[14,27].

3. RESULTS AND DISCUSSION

3.1. Short-time humidity test

Figures 2 and 3 illustrate the dependences of capacitance and conductance versus relative humidity for capacitors with barrier- and porous-barrier types of aluminum
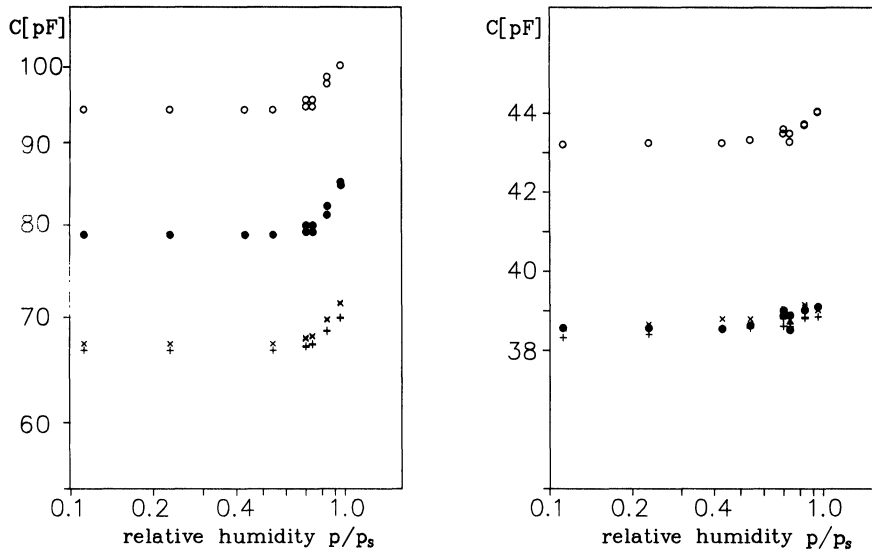
FIGURE 2   Capacitance characteristics of an Al_2O_3 capacitors versus relative humidity for barrier-type layer a) and porous-barrier layer b). Electrode materials as a parameter: (●) bump electrodes and (○) NiCr–Au–Cr film electrodes or (×) bump electrodes and (+) NiCr film electrodes of the complementary pairs of tested devices.
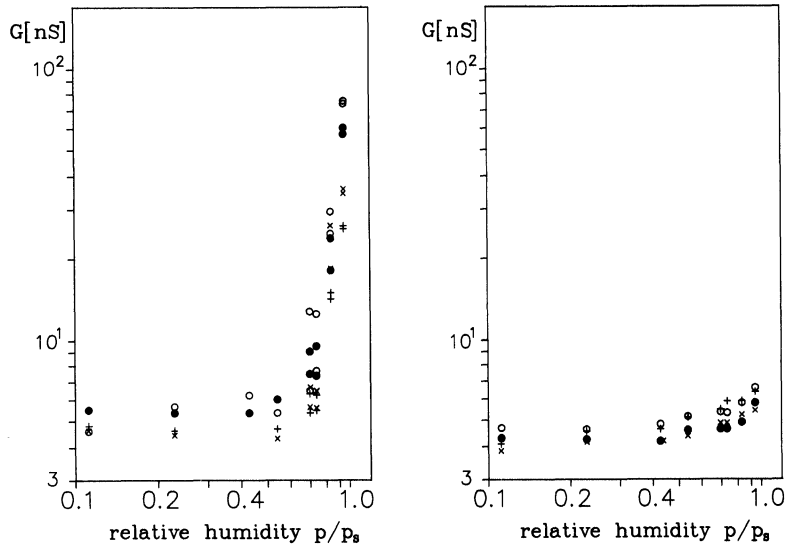

FIGURE 3   Conductance characteristics of an Al_2O_3 capacitors versus relative humidity for barrier-type layer a) and porous-barrier layer b). Electrode material as a parameter (see Fig. 2).

oxide layers. Both C and G parameters show similar dependences as a function of relative humidity but changes in the electrical conductance are distinguished.

According to the theory of humidity sensors[1] a plot on log-log coordinates of electrical conductance, G_p, versus relative humidity, p/p_s, yields a straight line according to the relation:

$$G_p = G_p^\circ \cdot (p/p_s)^m$$

where G_p° is a constant at fixed temperature, p/p_s is given by:

$$p/p_s = pH_2O/(pH_2O)_s$$

where p_s is the saturation pressure of water vapor.

For each device, independently of dielectric layer used and the material of the top electrode, the conductance and capacitance curves are represented in practice by two straight line segments: (1) a low-relative-humidity segment, and (2) a high-relative-humidity segment. The values of the measured slopes for each type of capacitor are given in Table 1. The transition points between low- and high-relative-humidity segments occur at relative humidity ranging between 54 and 75% RH. Variations in m-values can be explained by different surface conduction mechanisms. These mechanisms are affected by adsorption of water vapour molecules. The first layer of water molecules is chemisorbed to the cations incorporated into the surface[1-7]. At the low relative humidity the obtained m-values were below unity for both dielectric layers and all kinds of material electrode. This can be attributed

TABLE 1

A low- and high-relative humidity slope "m" for electrical conductance G_p versus p/p_s for Al_2O_3 capacitors

Al_2O_3 film type	Top electrode	RH range %	m	RH range %	m
barrier	solder bump	11–54	0.026	75–94	8.18
	NiCr–Au–Cr	11–54	0.203	75–94	8.19
	solder bump	—	—	75–94	7.99
	NiCr	—	—	75–94	7.19
porous-barrier	solder bump	11–54	0.155	70–94	0.889
	NiCr–Au–Cr	23–54	0.088	70–94	0.903
	solder bump	11–54	0.085	75–94	0.39
	NiCr	11–54	0.13	54–94	0.41

to fractional coverage by less than one water molecule per available cation site on the surface.

For porous-barrier oxide films the m-values are in the range from 0.085 to 0.15 and are independent of the top electrode materials. The differences in m-values can be the result of the measurement inaccuracy. For barrier oxide films the marked effect of electrode material is seen. The moisture effect on the capacitors with solder bump and NiCr electrodes is extremely small. On the other hand the presence of chromium lying direct on Al_2O_3 film causes a rise in humidity sensitivity. The mechanism can be similar as in ceramic humidity sensors[9-11].

At high relative humidity the m-coefficient for porous-barrier oxide layer remains below unity. The times two higher m-value for devices with Cr electrodes in comparison with that for devices with NiCr electrodes can be connected with processing. The preparation of a NiCr–Au–Cr multilayer requires the use of additional photolithography processes which could affect the higher humidity sensitivity by increasing the surface contamination[12]. However for barrier oxide layers the calculated m-values at the high relative humidity are about 8 and are similar to other humidity sensors. The lowest values of "m" are obtained for NiCr electrodes. This indicates that the NiCr layer protects the oxide layers from moisture better than solder bump contact. At higher relative humidity the sensors described by investigators exhibit large m-values ranging in magnitude between 5 and 14.

These large m-values suggest that the following physical mechanisms can take place: (1) adsorption of water vapour into the second and third molecular layers—physisorption, (2) dissociation of water molecules with protonic conduction, (3) electrolytic conduction connected with the presence of liquid water inside capillary pores. It is clear from the surface conductivity mechanisms that the pore diameter and the geometrical shape of the pores in alumina oxide as well as the concentration of the surface anionic groups are the dominant influences on moisture sensitivity[9-12]. These factors strongly depend on the nature of the electrolyte, its concentration and the current density of anodisation. It causes the humidity responses of sensors obtained by various investigators to be divergent.

As we were interested in reducing the moisture effect on the properties of capacitors the two stage technique of dielectric layer preparation was of interest. By choice of an electrolyte containing chromic acid, the low anion concentration incorporation into the porous oxide film was obtained. The use of the second step of anodisation using inactive and effectively waterless electrolyte (borate electrolyte) resulted in an increase in the thickness of the barrier layer and in the filling of the pores in the original film (densification process). Additionally the film oxide thickness were chosen to obtain a completely densified oxide layer. The capacitors with the porous-barrier layer showed considerable smaller changes of capacitance C and of loss tangent tgδ versus relative humidity than those observed for capacitors with single barrier-type oxide films (Fig. 4 and 5).

3.2. Long-time humidity test

During long-time humidity test the various degradation processes caused by the action of time, temperature and humidity can take place. The changes of parameters
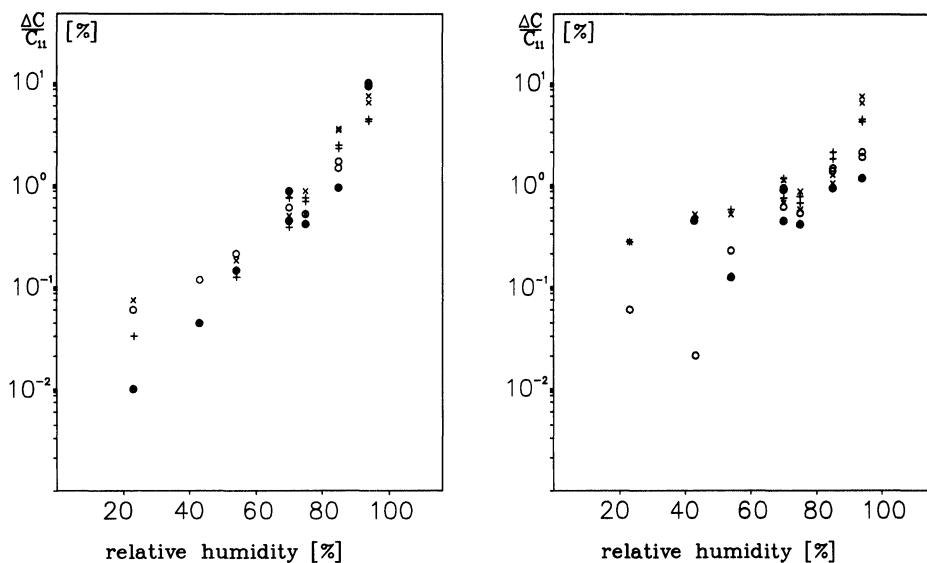
FIGURE 4   Relative changes of capacitance of an Al_2O_3 capacitors versus relative humidity for barrier-type layer a) and porous-barrier layer b). Electrode material as a parameter (see Fig. 2). Negative changes are distinguished by parenthesis.
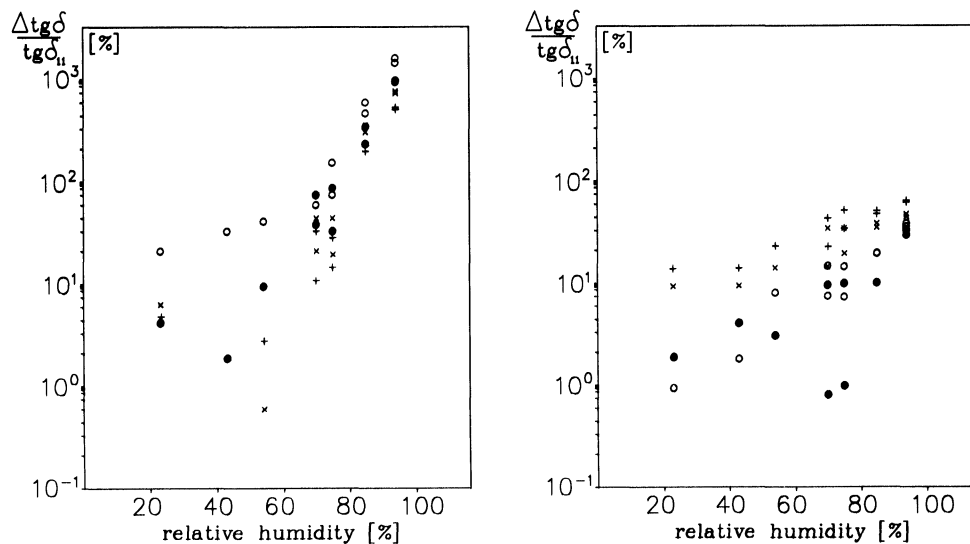

FIGURE 5   Relative changes of loss tangent of an Al_2O_3 capacitors versus relative humidity for barrier-type layer a) and porous-barrier layer b). Electrode material as a parameter (see Fig. 2). Negative changes are distinguished by parenthesis.

of capacitors connected with these processes can be reversible or irreversible. In the case of water vapour absorption the separation of these changes is difficult because of the high temperature required for water desorption. The data presented by Morimoto et al.[3] indicated that the water content decreased linearly up to about 400°C and decreased exponentially at higher temperatures during dehydration of oxides by heat treatment. At 800°C the remaining amount of hydroxyl groups was negligibly small. But such high temperatures would damage our capacitors. The reversible changes of parameters caused by the temperature can be distinguished by knowledge of the temperature dependence of the capacitance and conductance.

Behaviour of capacitors during prolonged exposure at 95% RH and 40°C is presented in Fig. 6.a) and b).

The values of capacitance and loss tangent and temperature coefficients of capacitance TCC and conductance TCG of capacitors before test are summarised in Table 2. In this test the great changes in capacitance and loss tangent were observed during the first 240 hours for both types of dielectric layers. In the case of barrier layer type there were no significant changes later. However for the porous-barrier layer after showing a maximum, the variations of parameters began to decrease and after 1344 hrs showed a negative values of the capacitance changes. The average changes of loss tangent for capacitors with porous-barrier layer were greater than those for barrier layer for the whole interval of time studied. Additionally in this test performed on high sample size a very high sensitivity to humidity in single elements with barrier layers were observed. This could be connected with stresses or microcracks obtaining in the Al_2O_3 films.

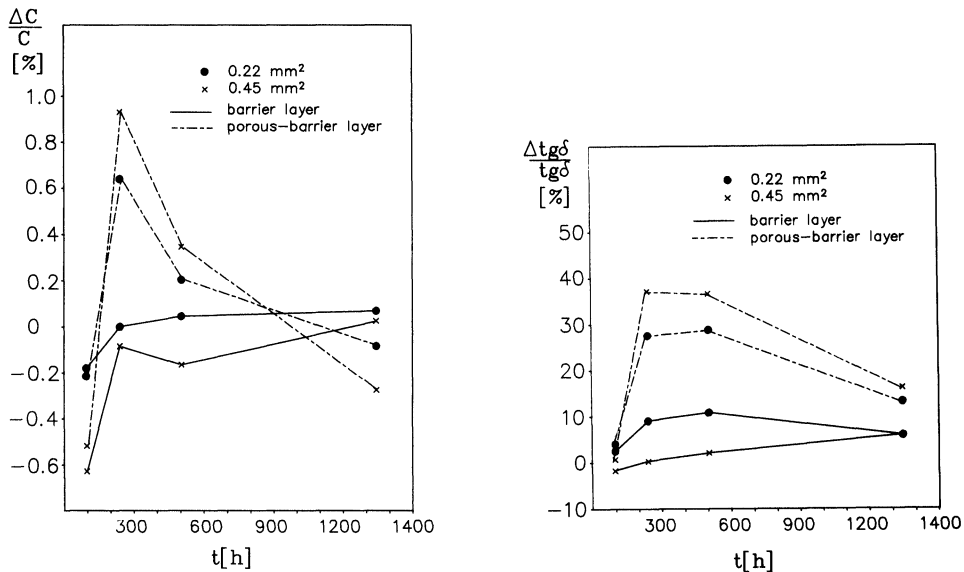For both dielectric layers the measured values of the temperature coefficients

FIGURE 6   Relative changes of electrical parameters of an Al_2O_3 capacitors versus time during long-time exposure to humidity of 95% RH at a temperature of 40°C. Barrier layer (solid curve) and Porous-Barrier layer (dotted curve). Changes of capacitance a) and changes of loss tangent b).

TABLE 2
Electrical parameters of an Al_2O_3 capacitors before long-time humidity test

Dielectric layer	Single capacitor area [mm²]	Sample size	Average capacitance C_0[pF]	Average loss tangent $tg\delta_0 \times 10^{-4}$	Temperature coefficient of	
					capacitance $\times 10^{-4}/°C$	conductance $\times 10^{-3}/°C$
barrier	0.22	172	48.10	72.9	4.64	7.4
	0.45	147	99.94	87.3	6.54	8.9
porous-barrier	0.22	177	21.54	74.8	5.39	5.5
	0.45	153	44.56	101.7	6.12	4.6

were similar. Temperature coeffcient of conductance was one order of magnitude greater than the temperature coefficient of capacitance—a result that is in a good agreement with previous date[14,15] for Al_2O_3 layers formed on inflexible substrates. However it should be noted that for Al_2O_3 sensors with Cu top electrode these coefficients have been found to be much greater and furthermore the temperature dependences are non linear[12]. These sensors were formed on thin Al-foil similar to our capacitors. The temperature coefficient of conductance was slightly higher for our barrier dielectric layer than for the porous-barrier Al_2O_3 layer. Both coefficients for the barrier layer structures showed high scattering of results which could be connected with stresses[28].

In our test the variation of ambient temperture was $\pm 2°C$ which gave an uncertainty of capacitance change in the range of $\pm 0.1\%$ and of loss tangent change below $\pm 1.5\%$. Since the observed changes (see Fig. 6) in the majority of cases can be described as irreversible, these changes probably resulted from ageing mechanisms connected with time-temperature acting in the presence of water vapour. However the changes originated from water desorption processes can be treated as reversible or irreversible dependently on the dehydration conditions especially at treatment temperature.

Time-temperature dependences of capacitor parameters can be ascribed to structural defect density changes related to the presence of ions in aluminium oxide[14,15,29]. For our capacitors aged in dry air at the temperature of 125°C up to 10000 hours the linear dependences of changes of capacitance versus time using a log-log plot gave a slope of about 0.25. The capacity changed by a few percent and the loss tangent by up to 30% for both dielectric layers. Both parameters showed negative changes[20,23]. Given the observed changes of capacitance and loss tangent up to 240 hrs (see Fig. 6) it is suggested that these could arise from the adsorption of water vapour on the capacitors as the dominant change mechanism. Measurements before measurement on the dehumidification of capacitors during storage in normal room atmosphere for few hours showed a much higher level of dehydration in the barrier-type layer than in the porous-barrier layer type. Also for capacitors with the barrier-type Al_2O_3 layer the heat treatment at the temperature of 125°C for 24 hrs performed after long-time humidity test showed a positive change in capacitance of about 0.2% and in loss tangent of about 20% in relation to these values before

test. This result testified that either in room temperature or in elevated temperature the dehydration is not complete and we are not able to divide the changes into reversible and irreversible parts. During long-time humidity test, catastrophic failures (short-circuit) for about 8% elements was observed. This value increased to 11% after heat treatment performed after the humidity test.

4. CONCLUSIONS

The new ingenious technique of Al_2O_3 dielectric layer preparation proposed affords the possibilities of producing capacitors with very low sensitivity to moisture in both the low- and high-humidity ranges. The results of short-time humidity test show that the dependence of electrical conductivity, G_p, on relative humidity p/p_s, is linear on a log-log scale up to a relative humidity value of 60% (the upper limit of the value reported for sensors). Above 60% a second linear region is observed. For capacitors with the porous-barrier type layer the slopes are below unity in the whole humidity range while for capacitors with the barrier-type layer this is only true in low-humidity range. Low sensitivity to moisture on a wide range of relative humidity is beneficial in capacitors.

In long-time humidity test the porous-barrier layer type show some what greater changes of parameters than the barrier layer commonly used for capacitors.

The influence of upper electrode material on moisture sensitivitiy varies. NiCr films as well as the solder bump contacts on NiCr–Au film give good protection from moisture action. On the other hand Cr electrodes are found to exacerbate the effect of moisture.

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