THIN FILM Al-Al₂O₃-Al CAPACITORS WITH DIELECTRIC LAYER FORMED AT 400°C

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A comparative study is made of Al_2O_3 layers formed at 400°C in molten KNO_3 and Al_2O_3 formed at room temperature in a common solution of ammonium pentaborate in ethylene glycol. At 400°C and constant current (0.5 mA/cm²) the linear anodization range is limited to 2.7 V by scintillation and local oxide breakdowns. Nonporous 200 Å thick (0.4 $\mu F/cm^2$) oxide layers were produced at 2.0 V (400°C) and 8 V (20°C). Electron diffraction indicated a γ-Al_2O_3 structure at an anodization temperature of 400°C and amorphous structure at room anodization temp. The initial values of tan δ were $100 \cdot 10^{-4} \pm 40 \cdot 10^{-4}$ and $400 \cdot 10^{-4} \pm 200 \cdot 10^{-4}$ respectively.

Capacitance and tan δ measurements during accelerated life test indicated that the films produced at 400°C are not superior to those formed at room temperature. In both cases a diffusion of metal at the metal-oxide interface seems to be the main ageing mechanism.

The internal electrical field measured by the C-V method was unchanged in γ-Al_2O_3 layers during the life test.

1. INTRODUCTION

There are some data indicating that it might be advantageous to produce thin film capacitors with an anodic Al_2O_3 dielectric based on Al electrode, similar to the well known Ta-Ta_2O_5-Me or Ta-Ta_2-MnO_2-Me structures. It seems that for applications at higher frequencies Al is superior to Ta because of a better conductivity. The purpose of this work is to provide the information necessary for comparison of two Al_2O_3 preparation methods, leading to different film microstructures. Our attention has been focused on very thin dielectric films, as we were interested in high capacitance density. The paper presented is the first part of a wider study devoted to factors affecting the properties of Al-Al_2O_3-MnO_2-Me structures.

2. EXPERIMENT

Al-film (≥99.99%) 6000 Å thick was evaporated on 7059 Corning glass substrates. Al_2O_3 layer 200 Å thick was prepared by anodization at two different temperatures, using two different electrolytes. At 400°C we have used molten KNO_3 a common solution of ammonium pentaborate in ethylene glycol being employed at room temperature. In both

cases, constant current (0.5 mA/cm²) – constant voltage type of anodization was performed.

In order to reach the proper Cl^- contamination level in both electrolytes (below 1 ppm) a routine purification process was conducted.
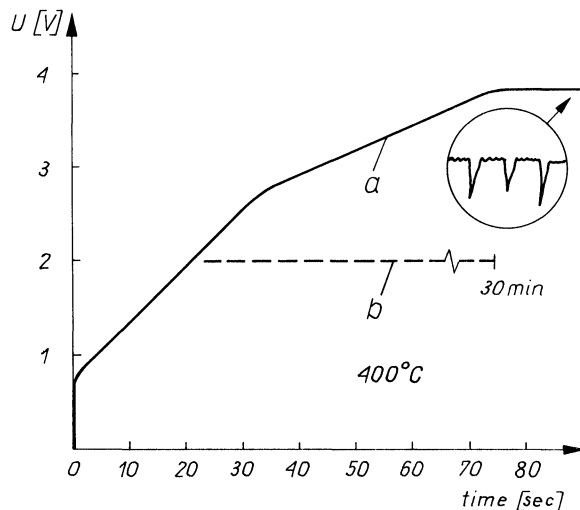
The study of the process at 400°C was started by

FIGURE 1   Voltage on Al_2O_3 anodic layer at 400°C as a function of time. a) at j = 0.5 mA/cm² = const. b) constant voltage period chosen for γ-Al_2O_3 films formation.

examining the voltage v.s. time behaviour at
$j = 0.5$ mA/cm^2 = const.

As shown in Figure 1, the linear range of anodic
oxide growth is limited to 2.7 V by film breakdowns.
That is why the voltage of 2.0 V was chosen for the
constant voltage anodizing period. The process has
been carried out in an Al tank used as a cathode.

For the process conducted at room temperature
we have selected the voltage of 8 V (constant voltage
period) as this value guarantees the same thickness.

For the evaporation of base and top electrodes we
have used mechanical masks giving 4 mm^2 of active
dielectric area. The top electrode was 500 Å thick.

Structural investigations of the Al$_2$O$_3$ film were
made by electron diffraction.

3.   RESULTS AND DISCUSSION

In contrast to some results published earlier[1,2] our
Al$_2$O$_3$ films obtained at 400°C are transparent
with no visible differences to the films commonly
produced at room temperature. Only in the case of
KNO$_3$ contaminated strongly by Cl$^-$ ions (at the level
above 10 ppm) did we obtain anodic layers black in
appearance, similar to those described by
Campanella.[1,2] A full comparison is difficult as in
our case the anodization voltage applied was
considerably lower, being in the linear part of voltage
v.s. time curve, j = const. (Figure 1).

The electron diffraction pattern showed a
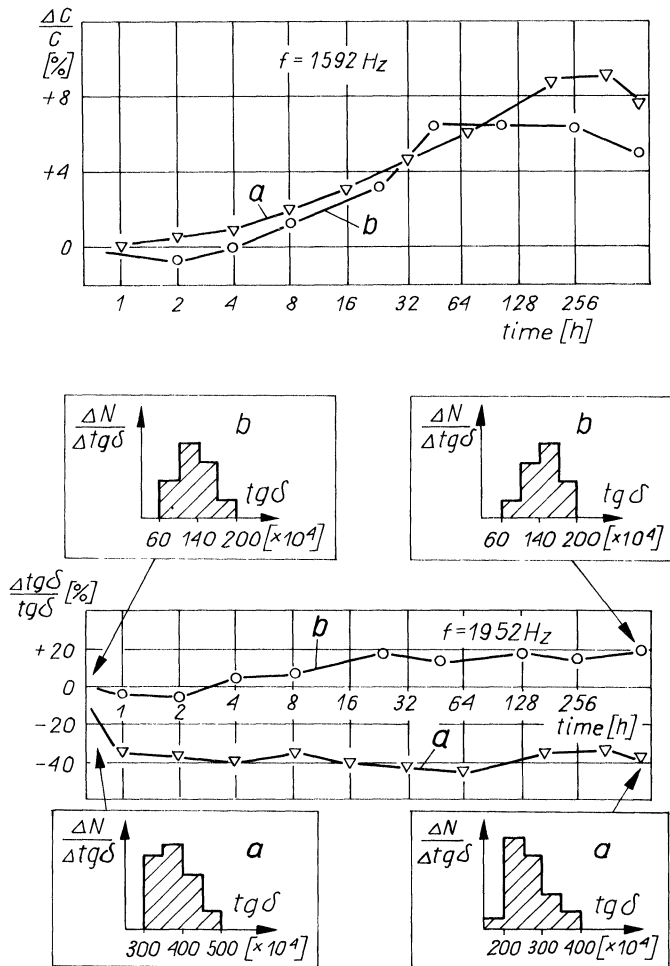significant difference in microstructure. At an

FIGURE 2   Relative capacitance and loss factor changes vs time. Ageing temperature 120°C; in air, f = 1592Hz
a) Amorphous 200 Å Al$_2$O$_3$ films. b) γ-Al$_2$O$_3$ films, 200 Å thick.
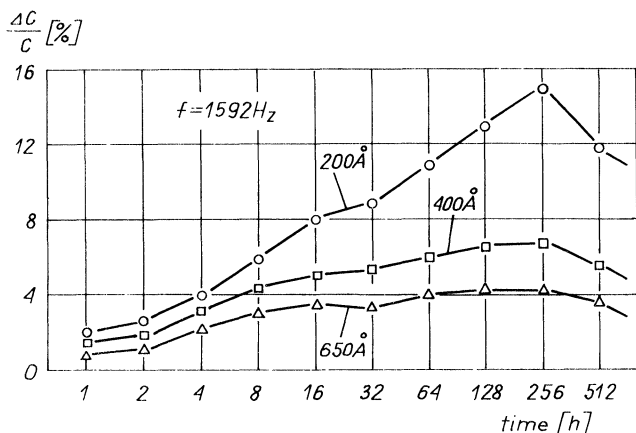
$\frac{\Delta C}{C}$ [%]

FIGURE 3   Accelerated ageing curves of Al-Al$_2$O$_3$-Al capacitors with different thicknesses of amorphous Al$_2$O$_3$ films. Ageing temperature 150°C; in air.
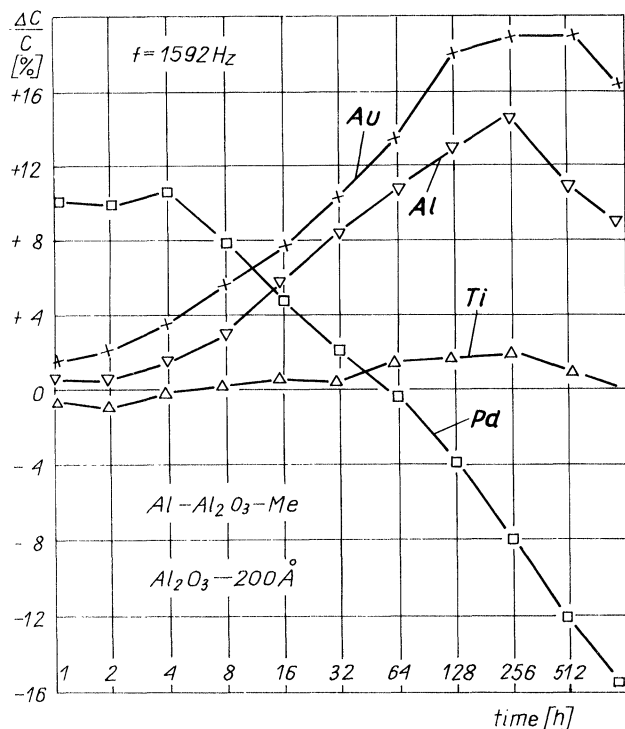

FIGURE 4   Accelerated ageing curves of Al-Al$_2$O$_3$-Me for different top electrode materials. Ageing temperature 150°C. Amorphous Al$_2$O$_3$ films.

anodizing temperature of 400°C, the γ-Al$_2$O$_3$ structure was obtained, while at room temperature the Al$_2$O$_3$ layers were amorphous.

The average initial value of capacitance is

0.4 μF/cm^2 with a tolerance of ±20% limited by masks. The average initial loss factor of capacitors with γ-Al$_2$O$_3$ is $100 \cdot 10^{-4}$, varying from run to run within $\pm 40 \cdot 10^{-4}$. For capacitors with a 200 Å thick amorphous Al$_2$O$_3$ film, it is $400 \cdot 10^{-4} \pm 200 \cdot 10^{-4}$.

This loss factor is surprisingly high but being strongly dependent on the thickness of dielectric film, it reaches a value below $100 \cdot 10^{-4}$ at about 700 Å.

The thermal ageing data are presented in Figures 2, 3 and 4. They include the average values of at least 20 samples selected from typical runs. Figure 2 shows also the loss factor distribution in two runs for different Al$_2$O$_3$ structures before and after thermal ageing.

The initially significant difference in tan δ is disappearing (Figure 2).

Capacitors with both types of dielectrics are about equally unstable (Figure 2). The stability improves with the increasing thickness of dielectric films (Figure 3). Nevertheless, the thickness of continuous γ-Al$_2$O$_3$ film obtained by this method is limited to about 250 Å (Figure 1). The stability is also strongly dependent on the material of the top electrode (Figure 4). The dependency of stability on dielectric thickness and on top electrode material are also
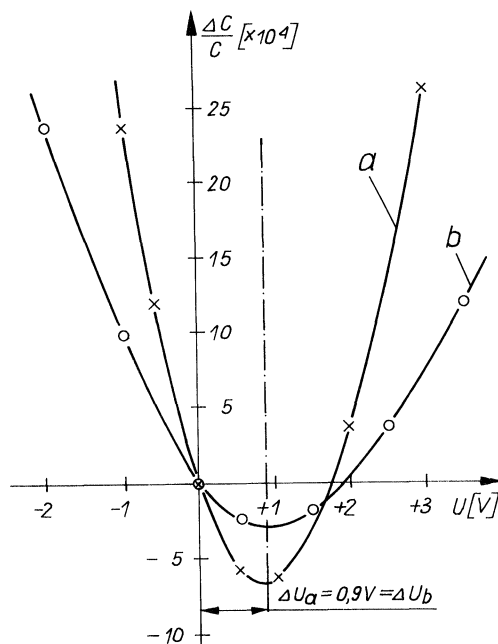

FIGURE 5   C-V curves of Al-Al$_2$O$_3$-Al capacitors with amorphous Al$_2$O$_3$ films 200 Å thick. a) Before ageing. b) After 100 h of thermal ageing at 120°C. The sign "+" refers to the base electrode; f = 1592 Hz.

FIGURE 6   C-V curves of Al-Al$_2$O$_3$-Al capacitors with
γ-Al$_2$O$_3$ films 200 Å thick. a) Before ageing. b) After 100 h
of ageing at 120°C. The sign "+" refers to the base electrode;
f = 1592 Hz.

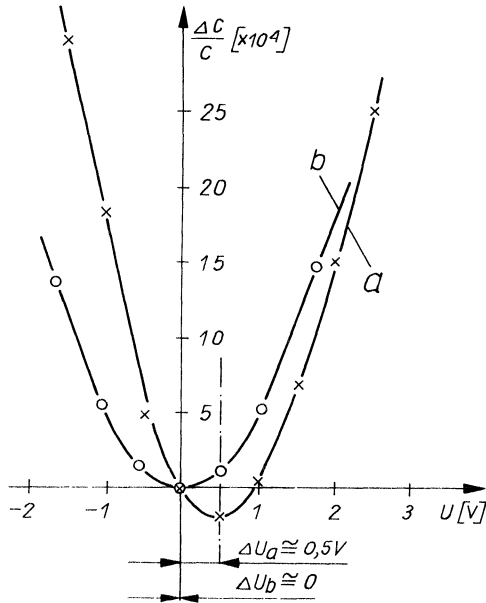manifested in the loss factor ageing curves which are
not shown here.[4]

Ageing behaviour of capacitors with both types of
dielectric is also sensitive to vapour energy during the
deposition of top electrode. The data presented are
relevant to the practically lowest vapour energy
(tungsten resistance sources; 2 A/sek). For the
samples evaporated at higher vapour energy the initial
parts of ageing curves are cut off, so that only their
decreasing portions are manifested. (Figure 3 and
Figure 4). This fact, together with the thickness

dependence (Figure 3) and that of the top electrode
(Figure 4) confirm the interfacial type of ageing
mechanism. This is true for low Al$_2$O$_3$ film thick-
nesses, while at higher thicknesses of about 2000 Å
the dominating ageing mechanisms are those inside
the dielectric layer.[3] The dipole moment of dielectric
film detected by the C-V method remains unchanged
in γ-Al$_2$O$_3$ films (Figure 5, ΔUa = 0.9 V), while in an
amorphous layer it decreases during the ageing
process to the undetectable level (Figure 6, ΔUb $\cong$ 0).
This is probably the most significant difference in
behaviour of capacitors with two Al$_2$O$_3$ films 200 Å
thick having a different microstructure.

4.   CONCLUSIONS

1) Adherent nonporous and transparent γ-Al$_2$O$_3$
oxide layers are obtained by anodizing in molten
KNO$_3$ at 400°C. Their thickness is limited to about
250 Å.

2) In Al-Al$_2$O$_3$-Al capacitors with 200 Å dielectric
films, the interfacial type of ageing mechanism is
dominant. Thus the capacitors with both type of
dielectric microstructure are almost equally unstable.

3) The γ-Al$_2$O$_3$ layers, in contrast to the
amorphous Al$_2$O$_3$ film produced at room tempera-
ture, exhibit a stable dipole moment.

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