Development of Temperature-Stable Thick-Film Dielectrics: I. Low-K Dielectric

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Abstract—A temperature-stable low-dielectric constant ($K \sim 10$) thick-film dielectric is developed. A dual frit approach proves to be an effective method in eliminating the pinhole problems in the fabrication of thick-film capacitors. Substrate bodies and diffusion of electrode and substrate ingredients into the dielectric are two major factors which affect the dielectric properties of the capacitors. The low-K dielectric developed in this study can work adequately from 25°C to 500°C, and at 500°C for an extended period of time.

INTRODUCTION

MICROELECTRONICS which is stable in a wide temperature range (e.g., 25°C to 500°C) is needed in many areas. Thick-film technology provides the most logical approach for developing passive electronic components that will perform adequately up to 500°C because thick-film components are processed well above 500°C. However, high-temperature processing does not automatically guarentee successful operation at lower temperature. Several studies demonstrate that few commercial systems for thick-film resistors and capacitors are marginally satisfactory at 300°C, but totally unusable in the temperature range 300°C to 500°C [1]–[4]. This is due to the fact that thick-film microcircuits are nonequilibrium systems that depend on a variety of complex physical and chemical processes which proceed to some degree of completion during high-temperature processing and are then frozen in when the circuit is cooled. The normal requirement of 125°C operation leads to the development of thick-film systems which perform very well below this temperature. However, some of the processes restart at higher temperatures, and their drive toward equilibrium produces irreversible changes in electrical properties.

The objective of this research is to develop a thick-film dielectric ($K \sim 10$) which is very stable from room temperature to 500°C. One important requirement for a dielectric material used in a thick-film capacitor of crossover is zero open porosity, since any open porosity would result in a shorted capacitor or crossover after the counter electrode is applied. The most straightforward method to achieve zero porosity is to have a continuous glassy phase present during the processing. Most or all of the glass phase could disappear later in the process, as would be the case for a glass ceramic. Hence, the approach employed is to develop a partially devitrified, loaded glass.

For a thick-film capacitor to be employed at 500°C for an extended period of time, the strain point of the glass should be high in order to maintain a rigid microstructure at 500°C. Two glasses are applied in this study, and they are 29 mol % PbO–36.9 mol % B_2O_3–20.4 mol % SiO_2–13.7 mol % Al_2O_3 (G1) and 21 mol % CaO–9 mol % BaO–38 mol % B_2O_3–12 mol % Al_2O_3–20 mol % SiO_2 (G2) [5], [6]. The selection of these glasses is based on the refractoriness and appropriate thermal expansion coefficients. The strain points for G1 and G2 are 475°C and 600°C, respectively. The thermal expansion coefficients of both glasses (G1: $65 \times 10^{-7}/°C$, G2: $64 \times 10^{-7}/°C$) are similar to that of the Al_2O_3 substrate ($66 \times 10^{-7}/°C$). This would minimize any thermal mismatch effect.

Temperature stability of the dielectric can be derived by two methods. One is through a temperature-compensated, multiphase dielectric, which was demonstrated to be valid for the TiO_2–$MgTi_2O_5$ system [7]. The other is through a careful selection of temperature-insensitive ingredients as well as an optimization of the fabrication processes. In this study both methods are investigated. Controlling parameters which are essential to the development of a temperature-stable thick-film dielectric are probed and discussed.

EXPERIMENTAL PROCEDURE

Dielectric formulations were prepared by combining appropriate amounts of α-Al_2O_3, γ-Al_2O_3, or TiO_2 with Frit G1 and/or Frit G2. The mixed powders were blended with 50 to 80 vol % screening agent consisting of 10 percent N–300 ethyl cellulose in butyl carbitol solvent for 2 h on a roll mill.

Engelhard A3770 mixed bonded Pd/Au and DuPont 4119 chemically bonded Au were selected as bottom and top electrodes, respectively, because they provide relatively smooth surfaces while retaining good adhesion and wire bond strengths for extended periods at high temperatures [8]. Engelhard A3770 was printed in appropriate patterns, dried at 150°C for 15 min, and fired at 1020°C for 8 min. Dielectric formulations were printed through a 200-mesh stainless-steel screen, allowed to level at room temperature, dried at 150°C for 15 min to remove the solvent and at 400°C for 15 min to remove the ethyl cellulose, and fired in the temperature range 800°C–1000°C for times varying from 8 to 35 min. In most instances, a second layer of dielectric was printed, dried, and fired in the same manner. The 4119 gold conductor pattern was then printed on the dielectric, dried at 150°C for 15 min, and fired in the temperature range 700°C–820°C for 10 min as a counter electrode to give a one square capacitor pattern (3 mm × 3 mm).
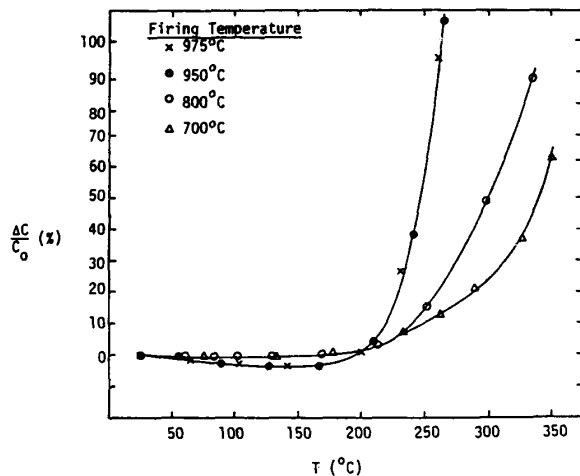
Fig. 1. Relative capacitance change of capacitors with 25 wt % TiO_2–75 wt % G1 dielectric as a function of temperature.
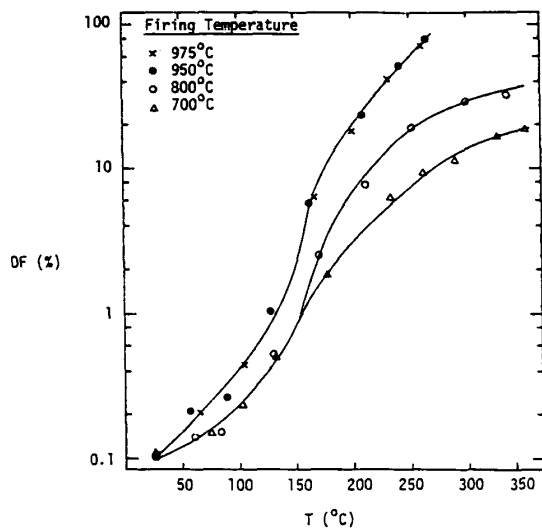

Fig. 2. Dissipation factor of capacitors with 25 wt % TiO_2–75 wt % G1 dielectric as a function of temperature.

RESULTS AND DISCUSSION

The first approach investigated for the development of a low-K dielectric is through a temperature-compensated, multiphase dielectric. The system selected is TiO_2–Frit G1 because rutile (TiO_2) shows a nearly linear, negative-temperature coefficient, and Frit G1 a nearly linear, positive-temperature coefficient, of dielectric constant over the temperature range of interest (25°C–500°C) [1], [2]. Calculations based on effective medium theory indicated that the composition 25 vol % TiO_2–75 vol % Frit G1 should have a dielectric constant of 13.6 at 25°C, 13.8 at 350°C, and 13.6 at 500°C. A thick-film formulation having this composition was prepared and capacitors were fabricated. Figs. 1 and 2 show the temperature dependence of relative capacitance change and dissipation factor of these capacitors for four different dielectric firing temperatures. The firing time of the dielectric was 12 min in

all cases. Both the dielectric constant and dissipation factor show dramatic increases as temperature increases, and the higher the dielectric firing temperature, the more temperature-dependent the dielectric properties become. The most probable explanation is that TiO_2 dissolved in Frit G1 during firing. Since Ti^{+4} is a highly polarizable ion, dissolution of TiO_2 in the glass would change the dielectric properties of the glass drastically. The higher the firing temperature, the more TiO_2 dissolves, and the dielectrics fired at higher temperatures would have a larger temperature dependence of dielectric properties as shown in Figs. 1 and 2. This approach is not feasible because firing at temperatures lower than 700°C would not yield capacitors stable at 500°C.

The second material system studied is glass G2 plus polycrystalline α-Al_2O_3. Alumina is selected because it has a dielectric constant ($K = 9.8$ at 1 kHz) similar to that of G2 ($K = 9.5$ at 1 kHz) [1], [2]. The similarity in the electrical properties should ensure the absence of interfacial polarization effects.

The Al_2O_3 should be added in sufficient quantity and as a powder with a sufficiently small particle size so that the equilibrium solubility of Al_2O_3 in the glass would be reached in a reasonable time at a firing temperature of ~1000°C. Alpha alumina monohydrate (AlOOH) was the initial choice for the source of Al_2O_3. The AlOOH loses its water of hydration at temperatures below those required for Frit G2 to flow and form a continuous phase, but it retains the extremely small particle size and high surface area characteristic of gamma alumina until it transforms to alpha Al_2O_3 at the firing temperature. Hence, it can assure that the equilibrium solubility is reached and that a uniform distribution of polycrystalline Al_2O_3 in the glass is achieved. As the dielectric is cooled from the firing temperature, some of the dissolved alumina will reprecipitate because the solubility of Al_2O_3 in the glass will decrease with decreasing temperature. This will give a dielectric with a final microstructure of a continuous glass phase containing small crystallites of Al_2O_3 which precipitated during cooling, and larger polycrystalline aggregates of Al_2O_3 which were undissolved. The presence of the crystalline Al_2O_3 will greatly inhibit flow of the dielectric during refire operations, which will be necessary in order to provide a counter electrode for capacitors or a conductive for crossovers.

Dielectric formulations with 5, 25, and 50 wt % Al_2O_3 relative to glass G2 (<38 μm) were prepared. 35 min at 1000°C was found to be the minimum firing time for these dielectric formulations. Among the three compositions, only the 25 wt % Al_2O_3 content ink produced satisfactory capacitors; all of the Al_2O_3 dissolved in the glass during processing of the 5 wt % Al_2O_3 formulation, and a severe pinhole problem was observed with the 50 wt % Al_2O_3 formulation.

The relative capacitance changes at 1 kHz for two capacitors made with 25 wt % Al_2O_3–75 wt % G2 dielectric are shown as a function of temperature in Fig. 3. The capacitors show a relatively small temperature dependence up to 250°C, but a rapidly increasing dependence with temperature between 250°C and 350°C. The relative capacitance change from room temperature to 350°C is 11 percent. The temperature depen-
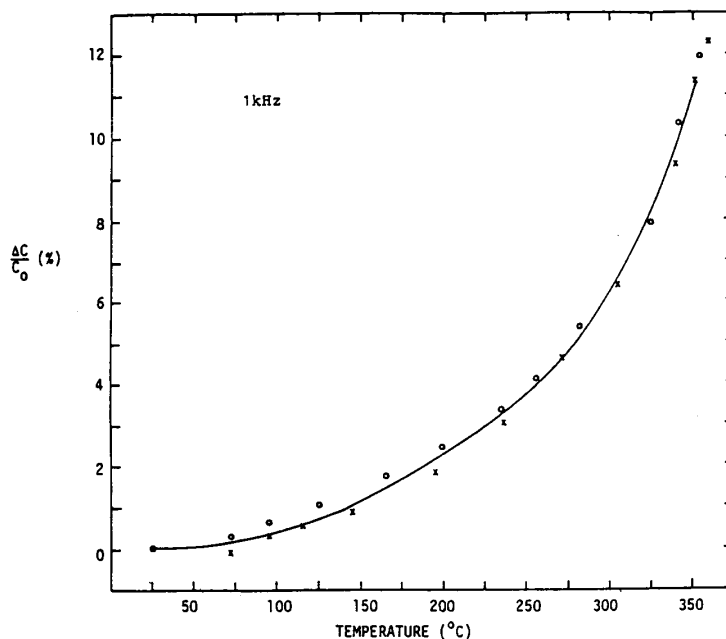
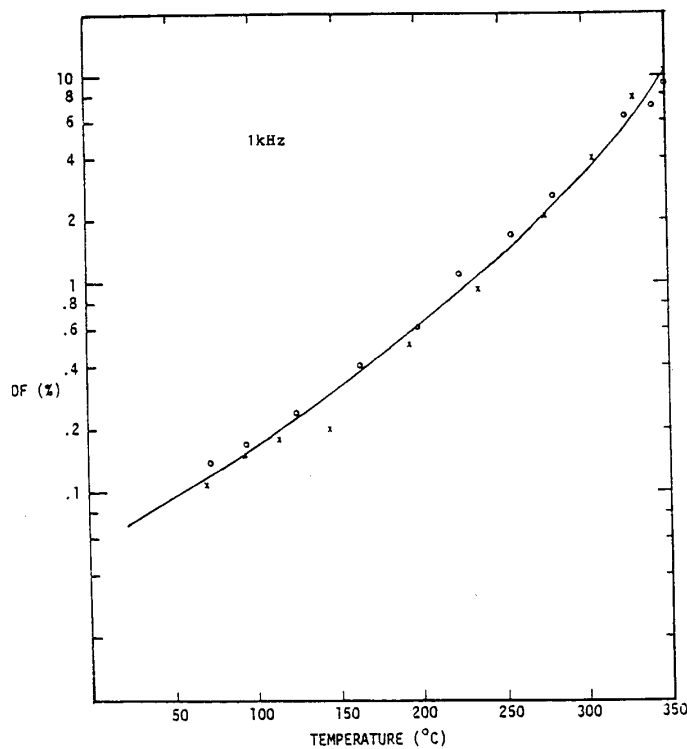Fig. 3. Relative capacitance change for two capacitors with 25 wt % Al_2O_3-75 wt % G2.

Fig. 4. Dissipation factor for two capacitors with 25 wt % Al_2O_3-75 wt % G2.

dence of the dissipation factor at 1 kHz is given in Fig. 4. The dissipation factor increases from less than 0.1 percent at room temperature to 10 percent at 350°C.

The 1-kHz capacitance and dissipation factor is independent of dc bias up to 500 V dc at room temperature. At 350°C, the dielectric constant remained the same up to 350 V dc, while the dissipation factor had a fluctuation rate of ±0.08 percent, which may have been caused by temperature fluctuations.

The temperature dependences of the capacitance and the dissipation factor for the test capacitors were both larger than
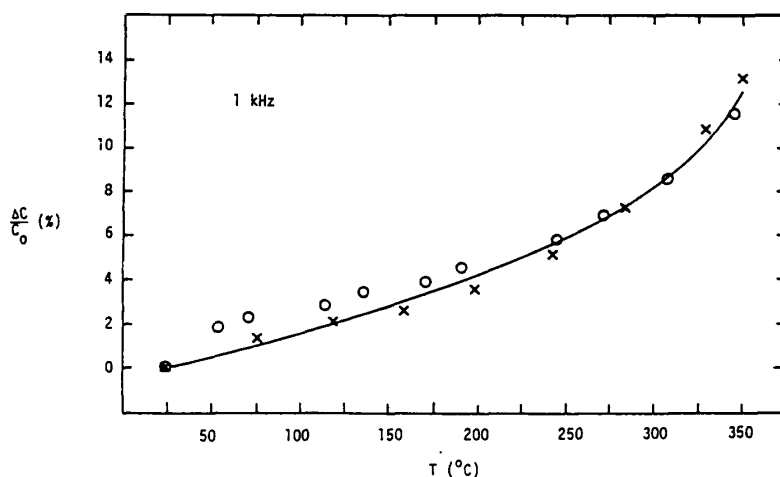
Fig. 5. Relative change in capacitance for two capacitors with dielectric 20 wt % Al_2O_3-80 wt % G2.
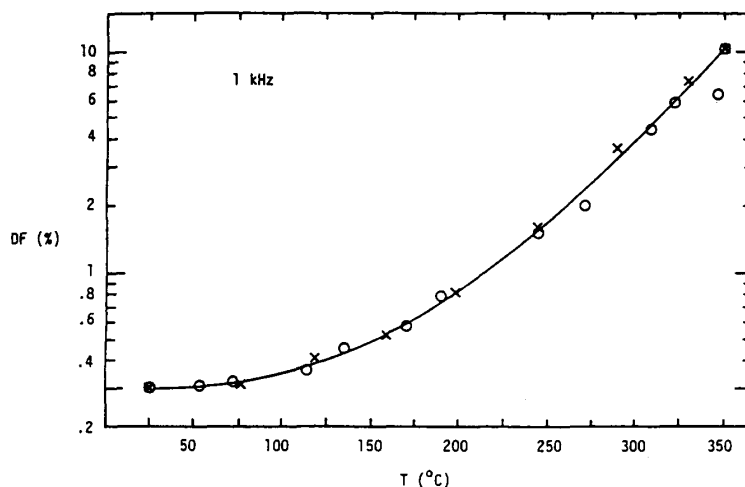

Fig. 6. Dissipation factor of two capacitors with dielectric 20 wt % Al_2O_3-80 wt % G2 as a function of temperature.

expected. The dielectric constant of Frit G2 should have changed by 5.3 percent from room temperature to 350°C and that of Al_2O_3 by 1.0 percent [1], [2], but the combination of the two gave a change of 11 percent shown in Fig. 3. There are many possible factors that cause the increase of the dielectric constant and dissipation factor as will be discussed later. One of them is that the Al_2O_3 was not completely converted from the gamma to the alpha phase. The dielectric properties of γ-Al_2O_3 as a function of temperature are not well known, but they would certainly be different from those of α-Al_2O_3 because of the different crystal structure. This may be one of the reasons that the 350°C dissipation factor of the capacitors deviates from what one would expect from the material system, i.e., 3.1 percent for Frit G2 and 0.4 percent for α-Al_2O_3. It is not possible to use X-ray diffraction techniques to determine the modification of Al_2O_3 present in the dielectric films because they are printed and fired on α-Al_2O_3 substrates.

Another difficulty with the low-K dielectric made from material system is the fact that the firing time, 35 min

minimum, is longer than desirable for commercial fabrication. One possible way to shorten the firing time is to use a smaller particle size Frit G2, and at the same time to reduce the alumina content. Figs. 5 and 6 show the relative capacitance change and dissipation factor of two capacitors with dielectric 20 wt % Al_2O_3-80 wt % G2, respectively. Frits of various sizes (10 wt % $<4 \mu m$, 10 wt %, 4-6 μm; 10 wt %, 6-10 μm; 20 wt %, 10-20 μm; 50 wt %, $<38 \mu m$) are diffused through the glass of these two samples. The firing condition is reduced to 15 min at 1000°C, which indicates that small glass particle ($<20 \mu m$) does help in eliminating pinholes.

Both the $\Delta C/C_0$ and DF of the 20 wt % Al_2O_3 samples are similar to those of the 25 wt % Al_2O_3 samples. Hence, AlOOH is abandoned as an Al_2O_3 source, and α-Al_2O_3 is employed in the following study.

One other approach to eliminate the pinhole problem is to replace some glass G2 ($<38 \mu m$) with glass G1 of smaller size (e.g., $<20 \mu m$). The strain point of glass G1 is lower than that of G2, which means that G1 has a lower viscosity than G2 does

TABLE I
SELECTED PROPERTIES OF G1, G2, AND α-Al$_2$O$_3$ [5], [6]

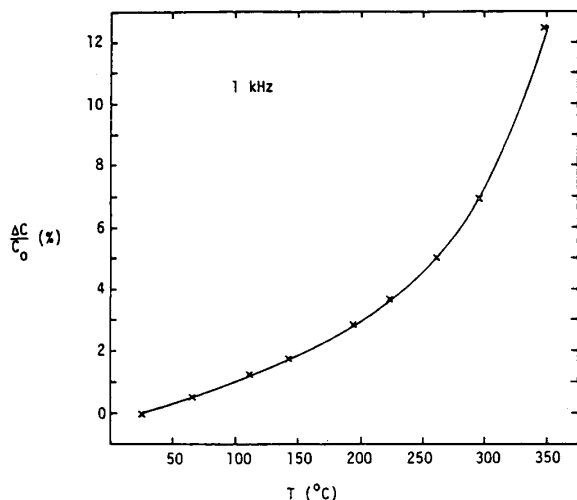| Property	G1	G2	α-Al$_2$O$_3$
$\Delta C/C_0$ (%), 1 kHz			
25°C–350°C	2.81	4.43	1.02
25°C–500°C	19.05	9.47	3.06
Dissipation factor, 1 kHz			
350°C		0.58	0.05
500°C	2.4	3.1	0.45

Fig. 7. Relative change in capacitance for capacitors with dielectric 50 wt % G1-25 wt % G2-25 wt % Al$_2$O$_3$ as a function of temperature.

Fig. 8. Dissipation factor of capacitors with dielectric 50 wt % G1-25 wt % G2-25 wt % Al$_2$O$_3$ as a function of temperature.

at the firing temperature. The presence of G1 will serve to fill in the interstices of the G2 structure, and help to form the continuous vitreous film in less time. Some selected properties of G1, G2, and α-Al$_2$O$_3$ are given in Table I.

The dielectric behaviors for compositions 50 wt % G1-25 wt % G2-25 wt % Al$_2$O$_3$ and 35 wt % G1-40 wt % G2-25 wt % Al$_2$O$_3$ are given in Figs. 7-10. The temperature dependences of the dielectric properties for capacitors made with both dielectrics were larger than expected based on the data given in Table I. The dielectric constants of Frits G2 and G1 should have changed by 4.4 and 2.81 percent, respectively, from room temperature to 350°C, and that of Al$_2$O$_3$ by 1.02 percent, but the combination of the three gave a change of 12.5 percent (Fig. 7) and 7 percent (Fig. 9). The dissipation factors of the three ingredients lead to an expectation of DF lower than 1 percent at 350°C, but the measured values were 10 percent (Fig. 8) and 3 percent (Fig. 10). It was also expected that capacitors made with the dielectric 50 wt % G1-25 wt % G2-25 wt % Al$_2$O$_3$ should give a smaller temperature dependence of capacitance than those made with 35 wt % G1-40 wt % G2-25 wt % Al$_2$O$_3$, because the former contains more Frit G1 than G2 and the temperature dependence of dielectric constant of Frit G1 is smaller than that of G2; however, the results show the opposite behavior (Figs. 7 and 9). Two possible explanations for the divergent behavior of the dielectrics and their ingredients are: interfacial polarization
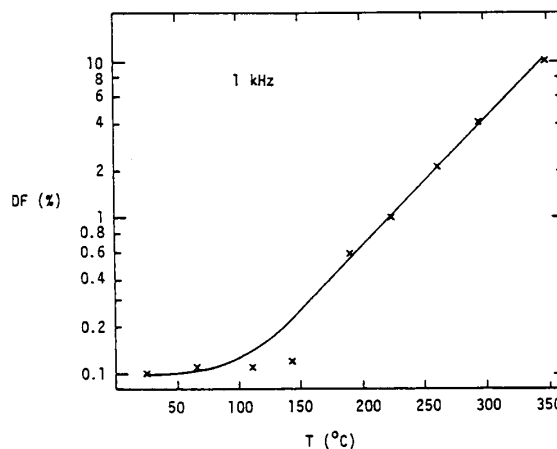
effects either at the electrodes or between phases; and changes in composition of one or more of the phases during processing. From the frequency dependence of the dielectric constant (Fig. 11) and dissipation factor (Fig. 12) of capacitors made with dielectric 35 wt % G1-40 wt % G2-25 wt % Al$_2$O$_3$ at 350°C, it was concluded that polarization effects at 1 kHz are not sufficiently great to cause the anomalously large dielectric constants and dissipation factors.

One possible way that the ingredients could change composition during processing is by interactions among themselves. To investigate this possibility, the ingredients were removed one at a time. First, Frit G2 was removed and a dielectric consisting of 25 wt % α-Al$_2$O$_3$-75 wt % Frit G1 formulated. The temperature dependence of the capacitance change and dissipation factor of capacitors made with this dielectric are shown in Figs. 13 and 14. These properties for the dielectric without Frit G2 show temperature dependences similar to those of dielectrics 50 wt % G1-25 wt % G2-25 wt % Al$_2$O$_3$ and 35 wt % G1-40 wt % G2-25 wt % Al$_2$O$_3$ (Figs. 7-10), and much greater than either α-Al$_2$O$_3$ or Frit G1 alone. Next, the α-Al$_2$O$_3$ was removed and a dielectric containing only Frit G1 formulated. Because of the lower viscosity of this formulation compared to ones containing crystalline Al$_2$O$_3$, the firing temperature for the dielectric had to be reduced to 900°C and for the counter electrode to 650°C. The temperature dependence of the capacitance change and dissipation factor of capacitors made with Frit G1 dielectric are shown in Figs. 15 and 16, and the frequency dependence of these properties in Figs. 17 and 18. The relative dielectric constant change from room temperature to 350°C was 7 percent (Fig. 15), which is more than twice the 2.8 percent change measured with a bulk sample of Frit G1. The small frequency dispersions (Figs. 17 and 18) rule out interfacial polarization as a major contributor, leaving a change in composition of Frit G1 during thick-film processing as the most likely cause of this effect.

There are three possible ways that the composition could change during processing: 1) impurities introduced during formulation preparation, blending, or screening operations; 2)
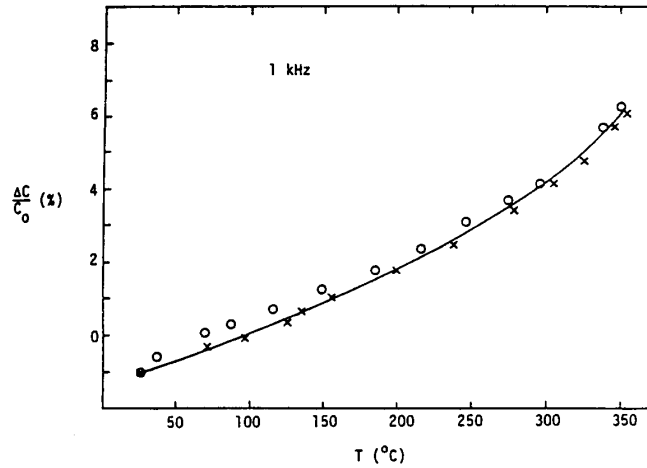
Fig. 9. Relative change in capacitance for capacitors with dielectric 35 wt % G1–40 wt % G2–25 wt % Al_2O_3 as a function of temperature.
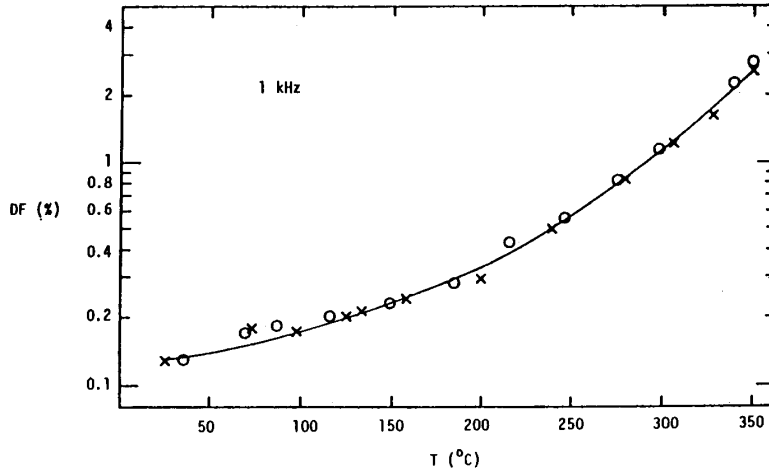

Fig. 10. Dissipation factor of capacitors with dielectric 35 wt % G1–40 wt % G2–25 wt % Al_2O_3 as a function of temperature.
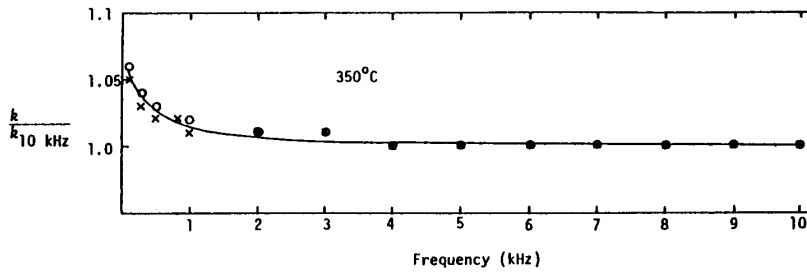

Fig. 11. Relative dielectric constant of capacitors with dielectric 35 wt % G1–40 wt % G2–25 wt % Al_2O_3 as a function of frequency.
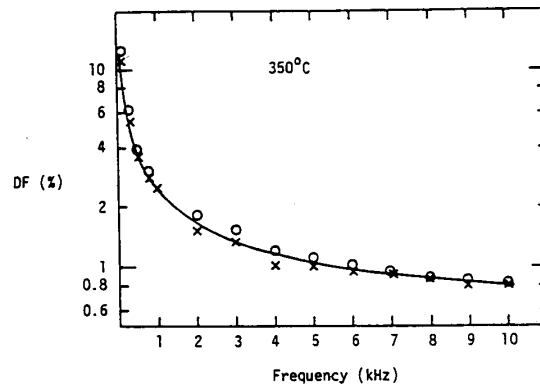
Fig. 12. Dissipation factor of capacitors with dielectric 35 wt % G1–40 wt % G2–25 wt % Al_2O_3 as a function of frequency.
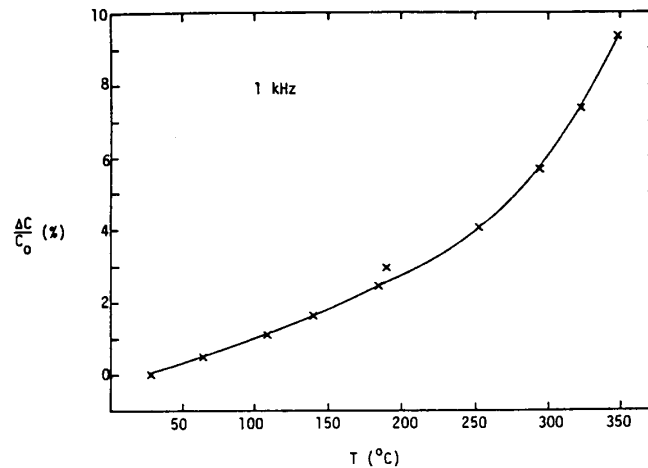

Fig. 13. Relative capacitance change of capacitors with 25 wt % α-Al_2O_3–75 wt % Frit G1 dielectric as a function of temperature.
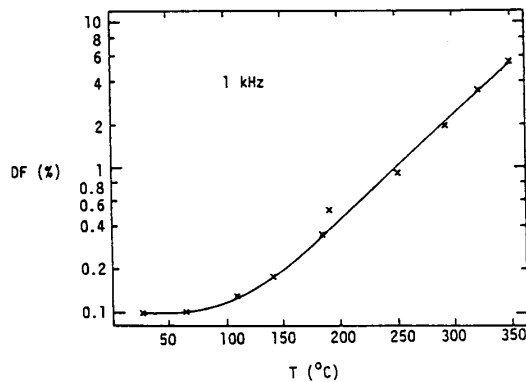

Fig. 14. Dissipation factor of capacitors with 25 wt % α-Al_2O_3–75 wt % Frit G1 dielectric as a function of temperature.

dissolution of the substrate in the glass during firing; and 3) diffusion of electrode ingredients into glass during firing.

Scrupulous attention was given to maintaining cleanliness and control during the formulation processing in order to minimize the first possibility. The substrate effect was studied by printing and firing the 35 wt % G1–40 wt % G2–25 wt % Al_2O_3 on three different substrates including two alumina substrates: AlSiMag 614 (96.5 percent Al_2O_3) and AlSiMag 772 (99.5 percent Al_2O_3), and Pt foils. The results are summarized in Table II.

Both the relative capacitance change from room temperature to 350°C and the dissipation factor at 350°C show lower scatter and lower average values for capacitors fired on AlSiMag 772 substrates. The result indicates that there is indeed an effect from the substrate. It is not known whether the difference in capacitor behavior are primarily due to differences in substrate surface chemistry or surface roughness, but the properties on AlSiMag 772 are sufficiently enhanced to warrant its use for high-temperature application.

Diffusion of electrode ingredients into the dielectric during firing was the third possibility which could produce an effect on the temperature dependence of the dielectric properties of the capacitors. Two approaches were used to investigate this possibility: the thickness of the dielectric film of the capacitor was doubled while keeping all other materials and processing conditions the same; and capacitors were prepared by printing and firing the dielectric on platinum foil.
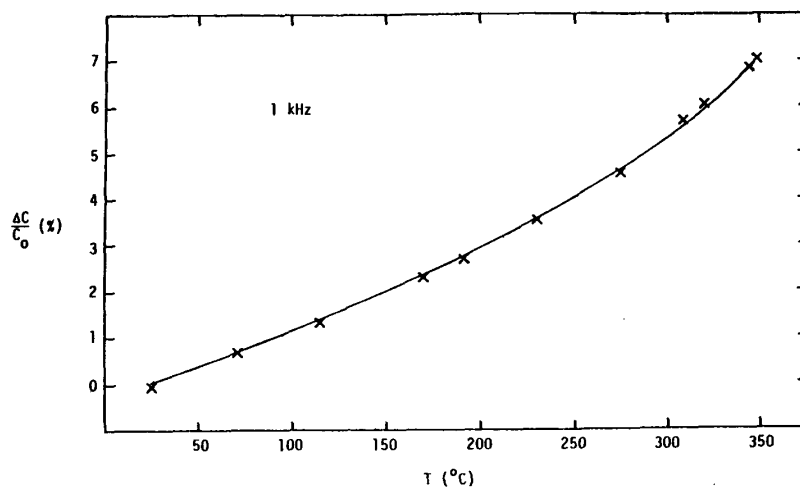
Fig. 15. Relative change in capacitance for capacitors with Frit G1 dielectric as a function of temperature.
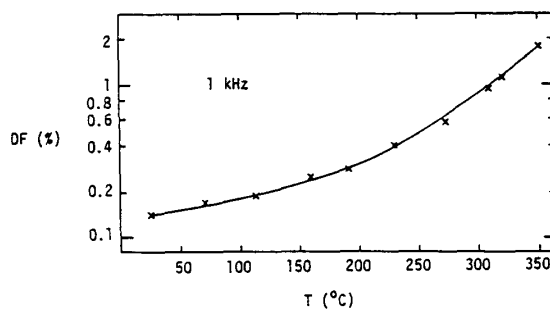

Fig. 16. Dissipation factor for capacitors with Frit G1 dielectric as a function of temperature.
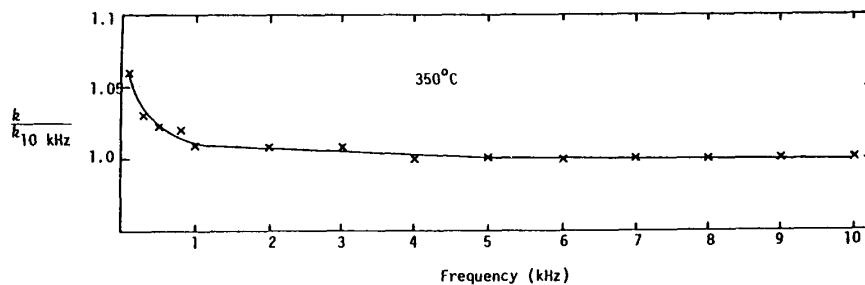

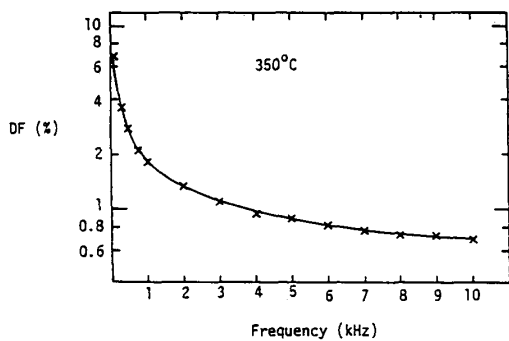Fig. 17. Relative dielectric constant of capacitors with Frit G1 dielectric as a function of frequency.

Fig. 18. Dissipation factor of capacitors with Frit G1 dielectric as a function of frequency.

Let x be the dielectric thickness of a capacitor, $C(x, t)$ the concentration of the electrode ingredients at position x and at time t, and $C(0, t) = C(h, t) = C_0$ the concentration of the electrode ingredient at the electrode. According to diffusion theory, the solution to the slab problem where $C(x, 0) = 0$ for $0 < x < h$ and $C(0, t) = C(h, t) = C_0$ where h is the slab thickness is given by

$$C(x, t) = C_0 - \frac{4C_0}{\pi} \sum_{j=0}^{\infty} \frac{1}{2j+1} \sin\left[\frac{(2j+1)\pi x}{h}\right]$$

$$\cdot \exp\left\{-\left[\frac{(2j+1)\pi}{h}\right]^2 DT\right\}.$$

TABLE II
COMPARISON OF 35 wt % G1–40 wt % G2–25 wt % Al_2O_3 CAPACITORS FIRED ON DIFFERENT SUBSTRATES

Substrate	Number of Capacitors Investigated	$\Delta C/C_{25°C}$ (%) 25°C–350°C	25°C–500°C	DF (%) 1kHz at 350°C	1kHz at 500°C
AlSiMag 614	11	5.88–10.53		1.8–7.6	
AlSiMag 772	8	4.46–5.98	12.4–14.5	0.6–1.0	13–14
Pt foil	2	4.1 and 5.0	8.1 and 10.2	0.35 and 0.6	2.3 and 6.0

TABLE III
COMPARISON OF 35 wt % G1–40 wt % G2–25 wt % Al_2O_3 CAPACITORS
WITH DIFFERENT DIELECTRIC THICKNESS, SUBSTRATE AlSiMag 772

Dielectric Thickness (μm)	Number of Capacitors Investigated	$\Delta C/C_{25°C}$ (%) 25°C–350°C	DF (%) 350°C, 1 kHz
50–75	8	4.46–5.98	0.6–1.0
125	5	4.0 –5.2	<0.2

The mean concentration inside the slab is given by

$$C_m(t) = \frac{1}{h} \int_0^h C(x \cdot t)\, dx = C_0 - \frac{8C_0}{\pi^2} \sum_{j=0}^{\infty} \frac{1}{(2j+1)^2}$$

$$\cdot \exp\left\{ -\left[\frac{(2j+1)}{1} \right]^2 Dt \right\}.$$

Thus the thicker the dielectric film (h) the smaller the effect of diffusion.

Table III gives the relative capacitance change and dissipation factors of capacitors with different dielectric thickness. Capacitors with thicker dielectric have better temperature stability. These results indicate that diffusion of electrode or substrate ingredients into the dielectric increases both the relative capacitance change and the dissipation factor.

Printing and firing the dielectric on Pt foil should eliminate any effect due to dissolution of substrate and diffusion of bottom electrode ingredients into the dielectric during firing. Capacitors fired on Pt foil do have lower capacitance change and dissipation factor as indicated in Table II.

Capacitors with dielectric 35 wt % G1–40 wt % G2–25 wt % Al_2O_3 are stored at 500°C, no apparent change in the dielectric properties is observed. This indicates that a temperature-stable low-*K* thick-film dielectric can be formulated successfully with dual frit approach.

CONCLUSIONS

1) Dielectric 35 wt % G1–40 wt % G2–25 wt % α-Al_2O_3 proves to be a very promising low-*K* dielectric for 500°C thick-film application.

2) The pinhole problem in fabricating thick-film capacitors can be eliminated with dual frit approach through the use of a glass with lower viscosity to fill in the interstices of the refractory glass structure.

3) Either substrate surface roughness or surface chemistry or both will affect the temperature dependence of the dielectric properties of the capacitors.

4) The dissolution of the substrate and/or the diffusion of the electrode ingredients during firing increase the relative change of capacitance and the dissipation factor of the capacitors.

5) A temperature-stable thick-film dielectric cannot be derived from the temperature compensation between dielectric properties of Frit G1 and TiO_2. The dissolution of Ti^{4+} into Frit G1 changes the dielectric property of the glass.

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