New Capacitor Dielectrics Covering K=2,000 to 12,000 for Printing and Firing Applications Below 1000°C

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Abstract

A new series of thick film capacitor dielectrics with dielectric constants from about 2000 to 12,000 and dissipation factors around 1% has been developed. The dielectrics are compatible with a wide range of conductors and can be processed in standard thick film furnaces at peak temperatures of 850°-980°C. The best results are obtained when these materials are terminated with specially developed silver based conductors and protected with a new one stage, low firing overglaze.

Key Words: Capacitor dielectric, Thick film, High K, Silver, Overglaze

Introduction

The continuing trend toward miniaturization of all electronic circuitry is driven by the concerted demands of reduced cost and increased performance. The development of conductive, resistive and dielectric materials that can be printed and fired to form high density interconnection for integrated circuit chips and reliable, compact passive components has contributed to the substantial progress made in achieving these goals.

Where high capacitance density is required however, chip capacitors are generally preferred over thick film. The low capacitance capability associated with thick film systems can be traced to low film densities. These, in turn, are the result of shrinkage constraints imposed by the substrate and the firing temperature limitation of about 1000°C (necessary for reasons of compatibility with associated thick film materials).

A number of approaches have been advanced to overcome the limited capacitance capability while taking advantage of the cost savings provided by thick film processing. These approaches generally involve the use of high K ferroelectric powders such as $BaTiO_3$ or lead-based relaxers [1-9]. Protective overglazes are normally applied to the resulting films since they usually are not fully dense [1-4, 12].

$BaTiO_3$-based systems benefit from small additions of glass which act to aid sintering and improve film adhesion and density. Further additions rapidly reduce K values, however, due to dilution of the ferroelectric phase and chemical reactions. Ikegami estimates that a K value of about 2,000 is the maximum obtainable from such systems [3].

More recently, lower firing high K phases have been developed from Pb-based Perovskites, commonly known as relaxers [6-11]. Many compositions occur in this structure type as do solid solutions of individual compounds [13]. Firing temperatures below 1,000°C are possible but sintering aids are still required to optimize fired density and adhesion to alumina substrates. Electrical properties are sensitive to composition which, in turn, is readily altered by firing in the presence of fluxes, conductors and conductor binder systems. Yasumoto et al, have reported a K value of 12,500 for a fluxed thick film relaxer used with a Ag/Pb conductor system [8]. Steinberg and Cooper report a K 3,000 relaxer employing a Ag/Pt conductor for RC networks [9].

This paper will discuss the properties of a new series of screen printable dielectrics formulated to provide high capacitance densities while retaining the advantage of thick film processing. These capacitors offer a wide range of dielectric constants with silver, platinum/silver, palladium/silver and gold electrodes and provide the performance and cost characteristics needed in advanced circuit applications.

Experimental

Standard thick film techniques were employed to prepare capacitor test samples on 96% alumina substrates. Capacitor structures consisted of a bottom conductor layer, followed by two layers of dielectric and one layer of top conductor. One or two encapsulent layers were applied to some samples. Conductor and overglaze screens were 325 mesh, 28 µm (1.1 mil) emulsion thickness. Dielectric screen was 200 mesh, 40µm (1.6 mil) emulsion thickness. After printing, each paste was allowed to level for a 10 minute period prior to drying at 125°C for 10 minutes. Dielectric and overglaze layers were printed with double passes to minimize pinhole formation.

Firing of the inorganic materials was performed in belt furnaces with cycle lengths of 40-50 minutes and10 minutes at peak temperature. All layers were separately fired. Organic encapsulant 240-SB (vide infra) was cured in a box oven at 150°C for 2 hrs.

The test pattern produced square parallel plate capacitor structures of 0.04 and 0.25 cm^2 areas. The larger pads were used for calculation of the dielectric constant in order to minimize the influence of edge effects. Fired dielectric thicknesses were typically 35µ (1.2 mil) between conductor pads.

Table 1 lists the properties of the conductor materials used in this study. The developmental products D-9916, D-9516 and D-8816 were specially formulated to optimize the electrical properties of the new capacitor dielectrics.

Table 2 lists the dielectrics and encapsulants together with their recommended firing temperatures. Dielectric properties of the D-4212 and D-4202 materials are dependent on the conductor choice and processing temperature as will be shown later in the paper.

Results and Discussion

Table 3 shows the results of firing D-4212 (the high K end member) at 900°C using standard silver (9912) and palladium/silver (9695) conductors. The silver terminated samples gave substantially higher dielectric constants (K) while the test pieces terminated with palladium/silver exhibited better dissipation factor (DF) and insulation resistance(IR) values. The breakdown voltages (BDV) of the two were similar.

This rather significant impact of conductor type was verified with other metallurgies. Further work showed performance characteristics could be improved for each conductor type by optimizing their formulation. Table 4 reports K versus temperature for a standard silver conductor, 9912, and an optimized developmental silver, D-9916. K values of nearly 12,000 are realized with D-9916 when fired at 900-930°C, an improvement of approximately 25% over 9912. Dissipation factors are also reduced below 1% and insulation resistance increases by about a factor of ten. Breakdown voltage is not affected.

Table 2. 4200-series capacitor dielectrics and compatible overglazes

Product Designation	Material Type	Function	Firing Temperature(s)
D-4212	dielectric	high K end member	850°-980°C
D-4202	dielectric	low K end member	850°-980°C
D-4039-C	vitreous overglaze	protective coating	525°-580°C
240-SB	polymer coating	protective coating	150°C

Table 1. Conductor properties

Conductor Designation	Metal Type	Fired Thickness (µ)	Sheet Resistance (mΩ/square)	Initial Adhesion Pull Strength (2mm x 2mm) (lbs)	Aged Adhesion 48hrs/150°C (lbs)	Solderability 62/36/2
9912	Ag	12	1.5	20	16	very good
D-9916	Ag	12	1.6	20	19	very good
9695	Pd/Ag	12	2.8	14	6	very good
D-9516	Pt/Ag	14	2.1	20	19	very good
D-8816	Au	12	2.4	11*	----	very good**

* wires attached to Au/Sn solder pad with 62/36/2 solder
**very good solderability with ESL 3601 Au/Sn solder

Table 3. D-4212 fired at 900°C

Conductor	K (1KHZ)	%DF (1KHZ)	IR(Ω) (100V)	BDV (V/25μ)
9912	9350	1.2	5×10^{8}	230
9695	4700	0.4	1×10^{10}	250

Table 4. Effect of different silver conductors on the properties of D-4212

Conductor/ Temperature	K (1KHZ)	%DF (1KHZ)	IR(Ω) (100V)	BDV (V/25μ)
9912/				
850°	6560	1.6	5×10^{8}	260
900°	9350	1.2	5×10^{8}	230
930°	9450	0.9	3×10^{9}	240
D-9916/				
850°	7340	0.9	5×10^{9}	280
900°	11,400	0.7	1×10^{10}	250
930°	11,700	0.7	1×10^{10}	250

Figure 1 plots the dielectric constant of D-4212 relative to conductor choice and firing temperature. The Ag/Pt D-9516 curve closely follows that of D-9916 while the Au D-8816 and Ag/Pd 9695 curves fall to K values just below 8,000 and 5,000, respectively. Dissipation factors (not shown) are all below 1% at room temperature. IR values are typically $10^{10}\Omega$ and BDV values are about 250V/25μm. These data are for capacitors without an encapsulant.

D-4202 was developed as a lower K capacitor paste blendable with D-4212 to provide a range of available dielectric constants. With a nominal K of 2,000, D-4202 uses a chemistry similar to that of D-4212 but with the addition of compatible lower K phases. Table 5 presents the electrical properties of D-4202 fired with D-9916 in the range 850-930°C. The temperature dependence of the dielectric constant is similar to that of D-4212 with a leveling in the 900-930°C range. DF's are now a little above 1% but IR and BDV are improved.

Table 5. D-4202 with D-9916 conductors

Firing Temperature	K (1KHZ)	%DF (1KHZ)	IR(Ω) (100v)	BDV (V/25μ)
850°	1650	1.2	2×10^{10}	270
900°	1850	1.2	3×10^{10}	300
930°	1800	1.1	5×10^{10}	320

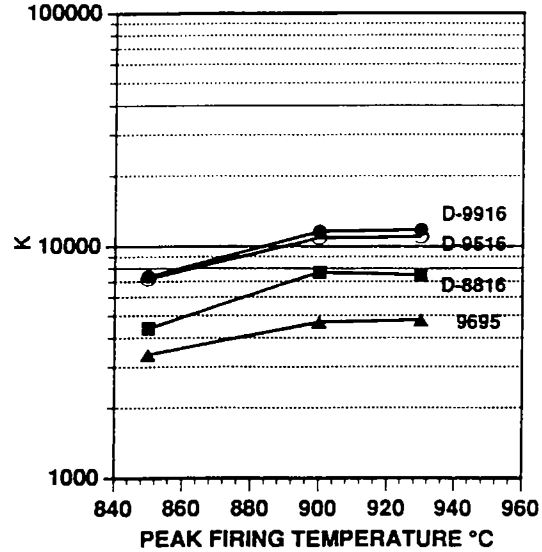

Figure 1 Termination effects on the dielectric constant of D-4212

Figure 2 plots the dielectric constant blending curve for D-4212/D-4202 mixtures with the D-9916 conductor. Linearity in K decreases in the blends with higher D-4212 concentration but a complete range of K values from 2,000 to 12,000 is seen to be available. Figure 3 shows the corresponding DF values.

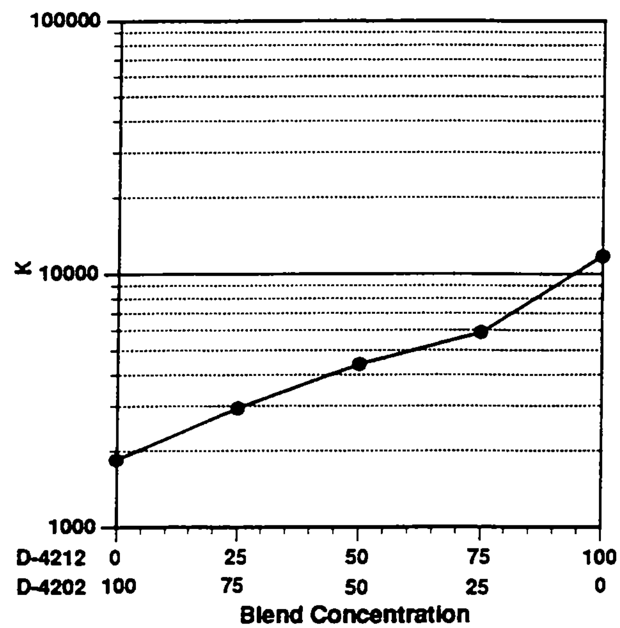

Figure 2 K values of D-4202/D-4212 blends fired at 900 °C with D-9916 conductors

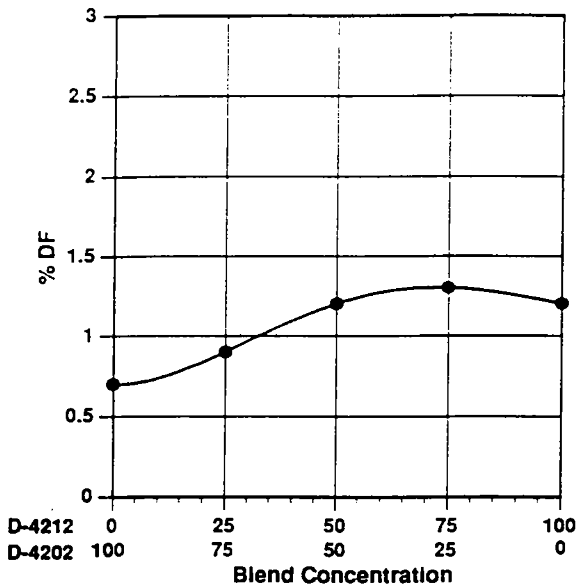

Figure 3 DF values of D-4202/D-4212 blends fired at 900°C with D-9916 conductors

High K ferroelectrics cannot tolerate large amounts of binders or sintering aids without suffering significant losses in dielectric constant. The compromise of allowing some porosity in order to achieve high K is acceptable when high performance encapsulation systems can be used to exclude moisture and other contaminants. Figure 4 is a 1300X SEM micrograph of D-4212 fired at 900°C with D-9916 silver conductor. This unpolished fracture cross section reveals a uniform grain size of 2-3μ and clearly shows porosity between the grains.

Both organic and inorganic encapsulants were evaluated as protectants for D-4212 and its blends. The polymeric 240-SB, cured at 150°C, resulted in less than a 1% decrease in the K of D-4212 while slightly improving its IR and BDV. However, since it is known that vitreous encapsulants outperform polymers in resisting moisture penetration[12], efforts were concentrated on evaluating the performance of D-4039-C as the overglaze for these capacitors. Table 6 lists the effects on the electrical properties of D-4212, D-4202 and a 50/50 blend when coated with two layers of D-4039-C at 580°C. K values drop a maximum of about 11% for the blend and about 5% for the end members. BDV values improve in all cases, especially for the two lower K compositions. Overall, the coating improves

Table 6. Overglaze effects on 900°C fired dielectrics with D-9916 terminations

Dielectric	K (1KHZ)	%DF (1KHZ)	IRΩ (100V)	BDV (V/25μ)
D-4212	11,400	0.7	5×10^9	280
D-4212*	10,800	0.6	2×10^{10}	385
D-4202	1850	1.2	3×10^{10}	290
D-4202*	1750	1.2	3×10^{10}	625
50/50 Blend	4250	1.3	1×10^{10}	300
50/50* Blend	3775	1.0	2×10^{10}	625

* Overglazed with two coats of D-4039-C fired at 580°C

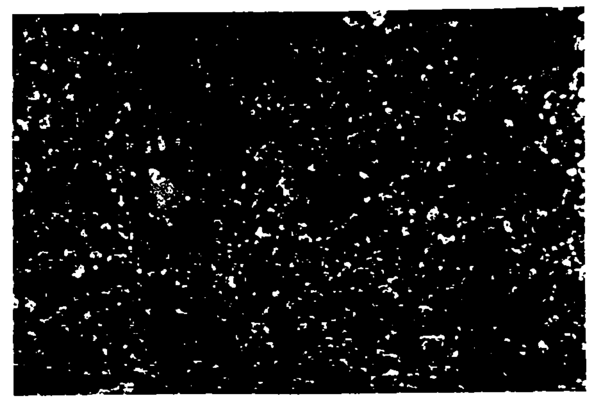

Figure 4 1300X SEM micrograph of D-4212 fired at 900°C

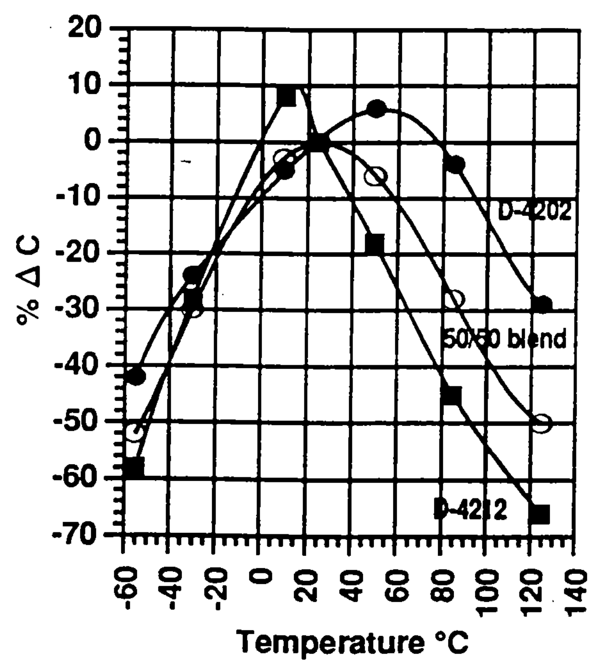

Figure 5 Effect of temperature on the capacitance of dielectrics fired at 900°C with D-9916 terminations

D-4202 possesses a denser body than does D-4212. This coupled with its lower capacitance value is the likely reason that the D-4202 performs well on the load life test even without overglaze.

Summary

A new series of high K thick film capacitor dielectrics has been developed. These are compatible with a wide variety of conductor metallurgies and fire around 900°C to allow cost-effective processing in standard thick film manufacturing schedules. Special silver, platinum/silver and gold conductor systems tailored to the chemistry of the dielectrics were formulated to optimize the performance of these materials.

A new, one stage overglaze has been shown to provide excellent environmental protection without the need for a conventional crystallizing buffer layer between the capacitor and the vitreous top layer. Reduction of the dielectric constant is very slight and firing temperatures are moderate (below 600°C).

The high capacitance density of up to 300 nF/cm^2 should allow these materials to find application in RC networks, RC chip components, capacitor arrays, delay lines, filters, high frequency connectors and other applications where large capacitance is needed.

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