Epoxy/$BaTiO_3$ ($SrTiO_3$) Composite Films and Pastes for High Dielectric Constant and Low Tolerance Embedded Capacitors in Organic Substrates

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Epoxy/BaTiO3 (SrTiO3) composite films and pastes for high dielectric constant and low tolerance embedded capacitors fabrication in organic substrates

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ABSTRACT

Epoxy/$BaTiO_3$ composite embedded capacitor films (ECFs) were newly designed for high dielectric constant and low tolerance (less than ±5%) embedded capacitor fabrication for organic substrates. In terms of material formulation, ECFs are composed of specially formulated epoxy resin and latent curing agent, and in terms of coating process, a comma roll coating method is used for uniform film thickness in large area.

Dielectric constant of $BaTiO_3$ & $SrTiO_3$ composite ECF is measured with MIM capacitor at 100 kHz using LCR meter. Dielectric constant of $BaTiO_3$ ECF is bigger than that of $SrTiO_3$ ECF, and it is due to difference of permittivity of $BaTiO_3$ and $SrTiO_3$ particles.

Dielectric constant of $BaTiO_3$ & $SrTiO_3$ ECF in high frequency range (0.5~10GHz) is measured using cavity resonance method. In order to estimate dielectric constant, the reflection coefficient is measured with a network analyzer. Dielectric constant is calculated by observing the frequencies of the resonant cavity modes. About both powders, calculated dielectric constants in this frequency range are about 3/4 of the dielectric constants at 1 MHz. This difference is due to the decrease of the dielectric constant of epoxy matrix. For $BaTiO_3$ ECF, there is the dielectric relaxation at 5~9GHz. It is due to changing of polarization mode of $BaTiO_3$ powder. In the case of $SrTiO_3$ ECF, there is no relaxation up to 10GHz.

Alternative material for embedded capacitor fabrication is epoxy/$BaTiO_3$ composite embedded capacitor paste (ECP). It uses similar materials formulation like ECF and a screen printing method for film coating. The screen printing method has the advantage of forming capacitor partially in desired part. But the screen printing makes surface irregularity during mask peel-off. Surface flatness is significantly improved by adding some additives and by applying pressure during curing. As a result, dielectric layer with improved thickness uniformity is successfully demonstrated. Using epoxy/$BaTiO_3$ composite ECP, dielectric constant of 63 and specific capacitance of 5.1nF/cm2 were achieved.

Keywords: embedded capacitor, polymer-ceramic composite, dielectric constant, tolerance

INTRODUCTION

Electronic systems are composed of a lot of active components and passive components. Passive components become of increasing interest because the number of passive components is steadily growing as the electronics industry is progressing toward higher functionality [1, 2]. Currently this large number of passive components is being surface-mounted on a substrate as discrete form. So they take up large area of a substrate and lower electrical performance and reliability due to long interconnection length and many solder joints, respectively. To solve these problems, embedded passive technology has been actively investigated.

Among passive components, special interest is given to capacitors, because they are used in large numbers for various functions, such as de-coupling, by-passing, filtering, and timing capacitors. In particular, great concern is concentrated on replacing discrete decoupling capacitors, which are used for simultaneous switching noise suppression, with embedded decoupling capacitors. It is because decoupling capacitors should be placed to chip as near as possible to reduce parasitic inductance.

One of the promising materials for embedded capacitors is polymer/ceramic composite, polymer filled with ceramic powders [3-5]. It utilizes high dielectric constant of ceramic powders and processability of polymers (low temperature process & low cost). In this study, barium titanate ($BaTiO_3$: BT), strontium titanate ($SrTiO_3$: ST) powder and epoxy resin were selected, because the powders are the most commercially available and well-known high dielectric constant ceramic powder, and the epoxy resin has a benefit of compatibility with PCB substrate.

Two most important requirements for embedded capacitor materials are high dielectric constant and low capacitance tolerance. In addition, good processability and low cost are also important. In previous work, we developed epoxy/ceramic composite ECFs to meet these requirements. In terms of material formulation, ECF is composed of specially formulated epoxy resin and latent curing agent. Transferable and B-stage film can be obtained using this formulation. And in terms of coating process, roll coating method is used for uniform film thickness on large area. There is no material waste in film formation.

Alternative material for embedded capacitor fabrication is polymer/ceramic composite embedded capacitor paste (ECP). In terms of materials formulation, it is a polymer/ceramic composite like similar to ECF, but in terms of a coating process, it uses a screen-printing method. Capacitor fabrication using the screen-printing method has an important advantage of forming capacitor locally in desired part through mask pattern. On the other hand, it is too difficult to obtain uniform thickness and flat surface.

In this paper, it will be discussed dielectric constant of BT & ST composites ECF with various powders at 100 kHz and high frequency region. Dielectric constants of epoxy/$BaTiO_3$ ($SrTiO_3$) composite ECFs were measured using the capacitor of MIM structure at 100 kHz. High frequency dielectric constants of ECFs were measured using cavity resonance method from 0.1 to 10GHz. Network analyzer is used to measure the reflection coefficient of some points of PCB with ECF layer. Measured results exhibit resonance frequencies associated with a rectangular cavity resonator consisting of six copper planes and a dielectric material. Since resonance frequencies correspond to resonance modes, we can measure several resonances and can estimate the relative permittivity at several frequencies.

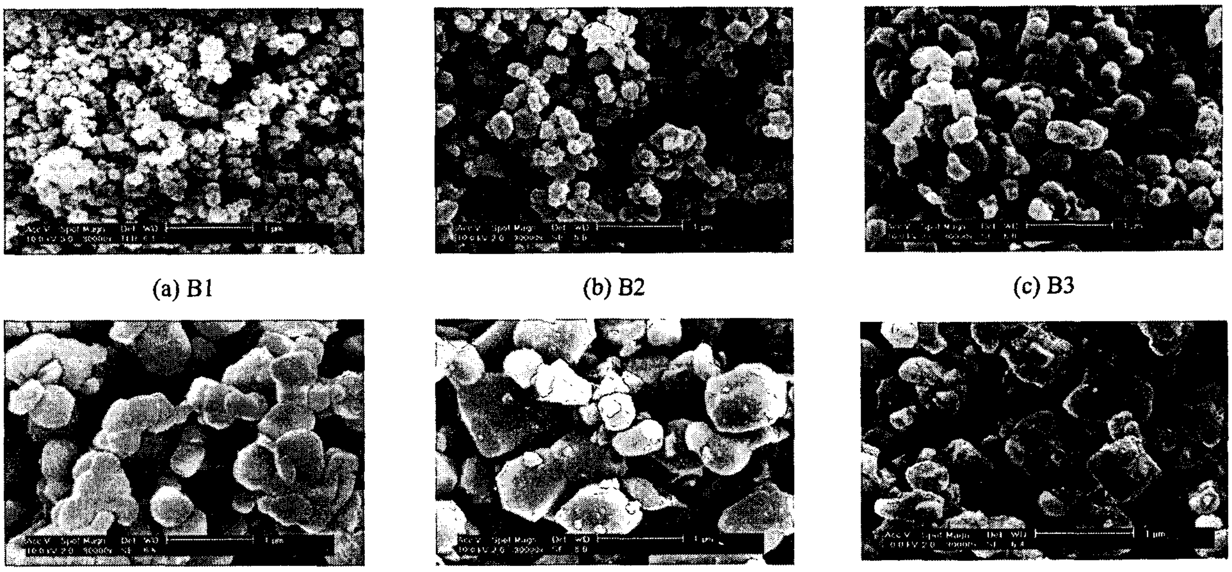
And we formulated embedded capacitor paste and formed polymer/ceramic composite capacitors using it. Pressure was applied during curing process to make dielectric layers flat and film thickness uniform. Capacitor fabrication using the embedded capacitor paste and the screen-printing method will be demonstrated.

Experimental Methods

A. Materials

$BaTiO_3$ and $SrTiO_3$ were chosen as ceramic particles. It is well known that dielectric constant of $BaTiO_3$ strongly depends on grain size or particle size. According to the previous reports, dielectric constant of $BaTiO_3$ bulk ceramics showed a maximum value of about 5000 when grain size was around 0.7~1㎛, and decreased drastically as grain size reduced.[6] Origin of the decrease of dielectric constant was attributed to the reduction of tetragonality with decreasing particle size and transition to cubic when powder size was less than 0.12μm.[7,8] Hence it is expected that particle size is very important parameter in selection of powder to get high dielectric constant. $SrTiO_3$ is well-known good dielectric properties due to its low microwave losses.

In this study, 5 kinds of $BaTiO_3$ (B1~B5) and $SrTiO_3$ (S1) powders commercially available with different particle size ranging 0.1 ~ 1.0 μm were used. Scanning electron microscope (SEM) images of the powders are shown in Fig. 1. All powders have nearly spherical shape as shown.


(a) B1 (b) B2 (c) B3

(d) B4 (e) B5 (f) S1

Fig. 1 SEM images of $BaTiO_3$ powders used for this study

Phosphate ester was used as a dispersant for the ceramic powders. Amount of the dispersant for each powder was adjusted by measuring the viscosity of a suspension containing each powder, dispersant, and solvent.

Mixture of bisphenol-A type and bisphenol-F type epoxies was used as a polymer matrix. As a curing agent of the epoxies, dicyandiamide (DICY) was used. DICY is a latent curing agent and curing does not proceed at room temperature due to high onset temperature over 100℃. Amount of DICY was 8.0 wt% of total epoxy weight. Mixture of methyl-ethyl-ketone (MEK) and Toluene was used for solvent.

B. Formation of ECFs

First suspension containing $BaTiO_3$ ($SrTiO_3$) powders, dispersant, and solvents was prepared in a plastic bottle. Ultrasonic power was applied to the suspension to break down $BaTiO_3$ powder agglomerates. Then the suspension was ball-milled for 2 days. After that, epoxies and curing agent were added to the suspension. After another ball-milling for two days, the mixed solution was coated on a releasing film using a roll coater as shown in figure 2. The ECF coated on the releasing film was dried sequentially before rewinding.

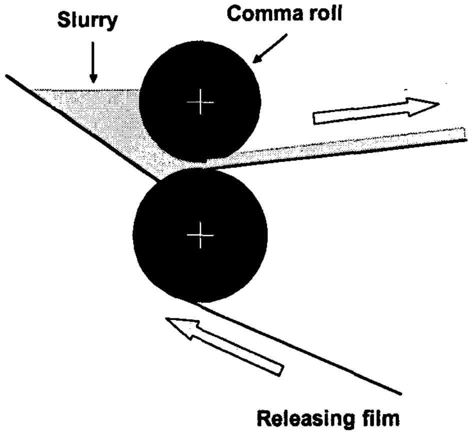


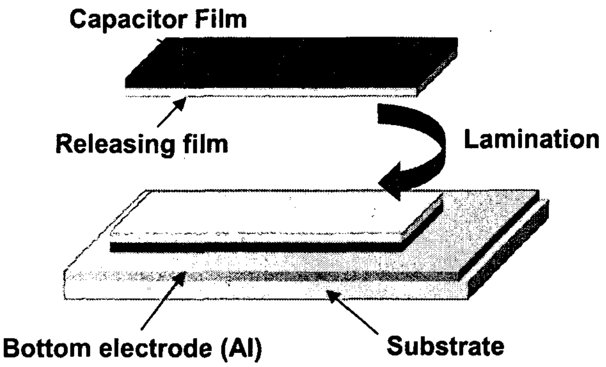
Fig. 2 Schematic diagram of film formation on releasing film

C. Sample fabrication and characterization

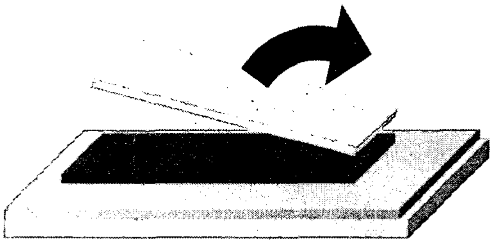
(1) For low frequency measurement

For fabrication of metal-insulator-metal (MIM) capacitors on PCBs, ECFs coated on the releasing film were dried at 100°C for 30 min in a vacuum oven to remove solvent residue. And then the dried ECF was laminated using heat and pressure at 180℃ and 50psi on a PCB where metal (Cu) blanket had been deposited for bottom electrode. After the lamination, the releasing film was removed and metal (Cu) top electrodes were deposited by sputtering using a shadow mask. Area of a metal dot for top electrode was 0.126㎠.

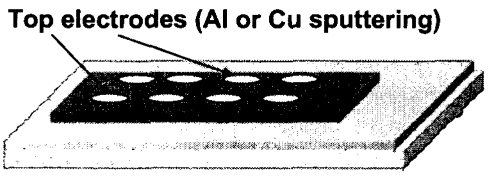
Capacitance and dielectric loss were measured at 100 kHz using HP 4284A LCR meter. Dielectric constant was calculated from the measured thickness and capacitance. For the accurate calculation of the dielectric constant of ECFs, only the films with the thickness tolerance below ±5% were used.



(a) Capacitor film lamination on a substrate



(b) Releasing film removal



(c) Top electrodes deposition by sputtering

Fig. 3 Metal-Insulator-Metal (MIM) capacitor fabrication process using ECFs on PCBs

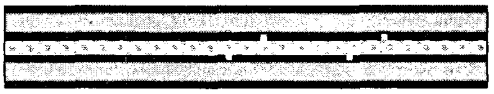
(2) For high frequency measurement

Principle of dielectric constant measurement by cavity resonance method was explained in detail in A. Namba's paper [9]. Consider a rectangular cavity resonator that is enclosed by six metal planes and is filled with dielectric material. If the height of the cavity is much less than a wave length, the distribution of electromagnetic fields is uniform in z direction. Therefore, a resonance frequency f_{mn} can be calculated using (1), where m and n are cavity-mode numbers, c is the speed of light, ε_r is the dielectric constant (or relative permittivity) of the dielectric material in the cavity, and a and b are the length and width of the resonator, respectively.

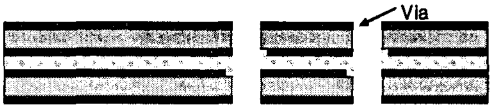
$$f_{mn} = \frac{c}{\sqrt{\varepsilon_r}} \sqrt{\left(\frac{m}{2a}\right)^2 + \left(\frac{n}{2b}\right)^2} \qquad (1)$$

Sample fabrication procedures are shown in Fig. 4. First, ECF is pre-laminated on 0.2mm thick copper clad laminate (CCL). In the same manner, another ECF pre-laminated CCL is prepared. The two CCLs are aligned and bonded using heat and pressure. Then via holes are drilled, and then Cu is deposited on via wall and four sides of PCB by plating. After that, using a photomask, copper is etched and probing pads are patterned. ECF thickness was about 50μm and $BaTiO_3$ particle volume fraction of ECFs varied from 0 to 55vol%.

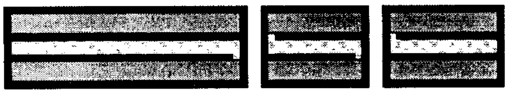
(a) ECF pre-lamination on CCL



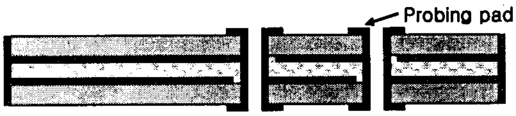
(b) CCL lamination



(c) Via formation



(d) Via & side wall plating



(e) Patterning of probing pads

Fig. 4 Fabrication procedure of PCB samples for high frequency measurement.

Dimensions of the PCB samples evaluated for this study were a (=60mm) × b (=60mm) × h (=0.5mm). Three probing pads, #1, #2 and #4 were located on the samples as shown in Fig. 5. #1 was located at the center of the PCB sample, #2 was located at x=a/4, y=b/4, and #4 was located at x=a/8, y=b/8. At a cavity-mode resonance, reflection coefficient has a dip. The magnitude of resonance depends on the position of the observing point. This can be used to identify cavity-mode numbers. Reflection coefficient S_{11} was measured in order to calculate the dielectric constant with an HP 8510C network analyzer. This equipment can measure S-parameter from 100MHz to 10GHz.

Equation (1) can be rewritten as following.

$$\varepsilon_r = \frac{c^2}{f_{mn}^2}\left[\left(\frac{m}{2a}\right)^2+\left(\frac{n}{2b}\right)^2\right] = \frac{c^2}{f_{mn}^2}\left[\frac{m^2+n^2}{4a^2}\right] \qquad (2)$$

Substituting the resonance frequency f_{mn} and mode numbers m, n into (2), the dielectric constant ε_r is calculated.

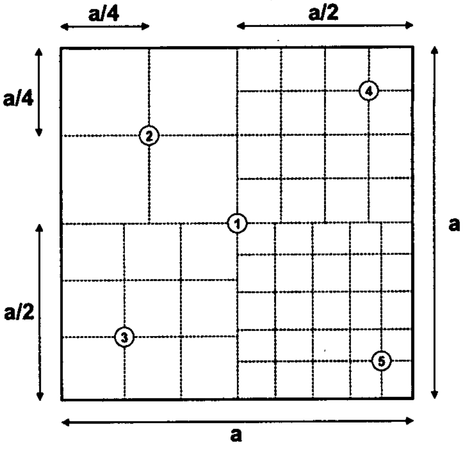


Fig. 5 PCB size and the probing pads location.

D. Embedded capacitor pastes (ECP)

Epoxy/$BaTiO_3$ embedded capacitor pastes were composed of epoxy-based polymer, $BaTiO_3$ powder, latent curing agent and some additives such as leveling agent and thixotropic agent. $BaTiO_3$ powder used for ECP formulation is the same used for ECF fabrication. Volume fraction of $BaTiO_3$ powder was fixed at 0.5 after solvent drying. Solution of polyacrylates was used for leveling agent. DICY was used as a curing agent. The composition of ECP is summarized in Table 1.

Table 1 Composition of ECP.

	ECP	Remark
Bisphenol-A liquid epoxy	3	Volume ratio
Additive polymer (M.W. ~ 170,000)	2	
Solvent (b.p. 228°C)	12	
Dispersant	1wt%	of total paste
Leveling Agent	1wt%	
Curing Agent DICY	8wt%	of resin
$BaTiO_3$ powder	50vol%	

The specifications of printing mask are 250-mesh and

30μm emulsion thickness and opening size is 4mm×4mm square. ECP was screen printed on Cu-plated FR-4 substrate for demonstration. Al-deposited glass substrate for more accurate dielectric constant measurement. Printed dielectric layer was dried at 120°C for 20 minutes. Afterward, 50psi pressure was applied at 200°C for 30 minutes in a laminator to improve flatness of the dielectric layer.

Cu top electrodes with 1μm thickness were formed on cured dielectric layer by sputtering. Capacitance was measured at 100 kHz AC field. Dielectric constant was calculated from the capacitance data and thickness data.

Result & Discussion

A. Dielectric constant of BT & ST ECFs

Figure 6 shows the variation of the dielectric constant of ECFs with various volume fractions of BT & ST powders. The dielectric constant of ECFs increases, as the amount of powder increases. However, at 55~60vol% it reaches a maximum value, and then decreases with further powder addition. This decrease in dielectric constant is due to the voids or the pores formed in film to accommodate the excess powders over the theoretical maximum packing density.

From Fig. 6 we can also find BT particle size effect on dielectric constant of ECF. The ECF fabricated using B4 (0.83㎛) shows a maximum dielectric constant. Below this size, the dielectric constants decrease as BT particle size decreases. But the dielectric constants of the ECF fabricated with B5 are smaller than those with B4. Variation in dielectric constant is mainly due to the change of the dielectric constant of BT powders, and this change is due to variation of tetragonality. Therefore, it is thought that B4 (0.83㎛) has the highest dielectric constant among the 5 powders. Below or above this size, the dielectric constant of BT powder decreases. At the same reason, the dielectric constants of the ECF fabricated with S1 are smaller than those of B1. Because $SrTiO_3$ powder has no tetragonality due to cubic-perovskite structure, dielectric constant of ST powder is much smaller than that of BT powder.

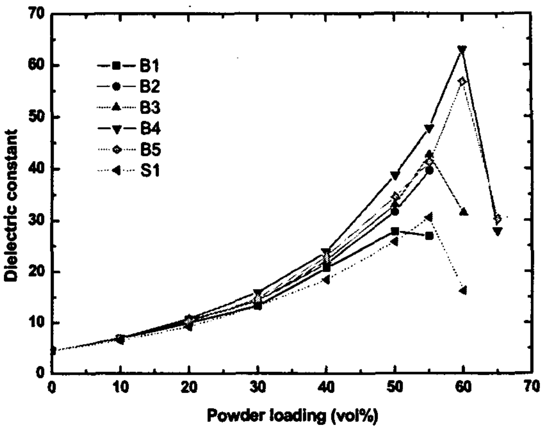
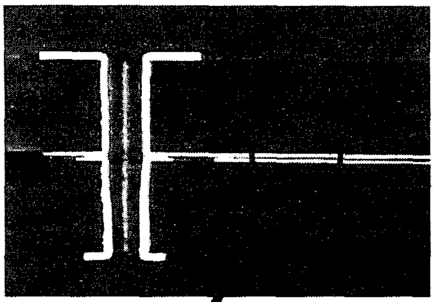


Fig. 6 Dielectric constant changes with BT & ST particle loading

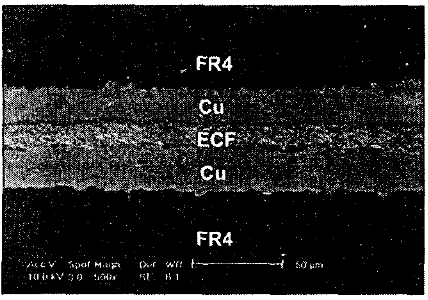
B. Measurement of high frequency dielectric constant of ECFs

Cross section images of embedded PCB with a capacitor layer observed using optical microscope and SEM are shown in Fig. 7 (a) and 6(b), respectively. Through hole via and ECF sandwiched between Cu electrodes are shown in these figures.

Fig. 8 shows the measured reflection coefficient at locations #1, #2 and #4 for epoxy film without BT powder. Resonance mode numbers (m,n) for each resonances are indicated in the figure. The first resonance mode is TM_{11} and the second is TM_{12}. For the TM_{11} mode, the resonance measured at location #1 in the center of the sample is stronger than at location #2. On the other hand, for the TM_{12} mode, no resonance was observed at location #1. This is because probing position #1 is located at a point where the distribution of E_z is maximum for the TM_{11} mode and null for the TM_{12} mode. Comparing the magnitude of the reflection coefficients at location #1 with those at location #2, each resonance mode can be identified.



(a) Though hole via in the embedded PCB (×50)



(b) Capacitor layer in the embedded PCB (×500)

Fig. 7 Cross section images of the embedded PCB for high frequency measurement

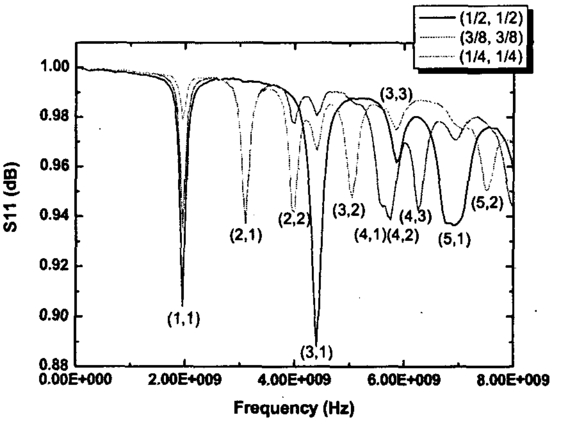


Fig. 8 Reflection coefficient (S_{11}) measurement result: epoxy

Substituting the measured resonance frequency and the identified mode numbers into (2), relative permittivity of the dielectric material at each frequency is obtained. Table 2 shows the values of the resonance frequencies and the corresponding values of relative permittivity for the epoxy film and the 20vol% ECF.

Table 2 Resonance frequency, mode number, and calculated dielectric constant.

Mode number	f_{mn} (Hz)	ε_r
(1,1)	6.75E+08	27.43481
(2,1)	1.08E+09	27.04164
(2,2)	1.38E+09	26.44628
(3,1)	1.55E+09	26.01457
(3,2)	1.75E+09	26.53061
(4,1)	2.00E+09	26.5625
(3,3)	2.08E+09	26.12861
(4,2)	2.18E+09	26.42357
(5,1)	2.50E+09	26
(5,2)	2.63E+09	26.30385
(4,4)	2.78E+09	25.97192
(5,3)	2.85E+09	26.1619
(6,1)	2.98E+09	26.1281
(6,2)	3.13E+09	25.6
(6,3)	3.28E+09	26.22225
(5,5)	3.50E+09	25.5102
(7,1)	3.50E+09	25.5102
(6,4)	3.53E+09	26.15563
(7,2)	3.55E+09	26.28447
(7,3)	3.73E+09	26.12495
(6,5)	3.83E+09	26.05835

Relative permittivity calculated in this manner is plotted with frequency in Fig. 9 and Fig. 10 about different BT powders. Additional data points about the dielectric constant measured at 1MHz using LCR meter is shown together in both figure.

Fig. 9 is shown the dielectric constant changes of the B1 (0.1μm), B3 (0.3μm), B5 (0.97μm) 20vol% ECF with frequency. The dielectric constants are maintained at constant values as frequency increases up to 9GHz. But at 9GHz abrupt change in dielectric constant which is called dielectric relaxation is shown about all the powders. It is thought that the relaxation is due to changing of polarization mode of $BaTiO_3$ powders with frequency, transferring from dipole polarization to ionic polarization region.

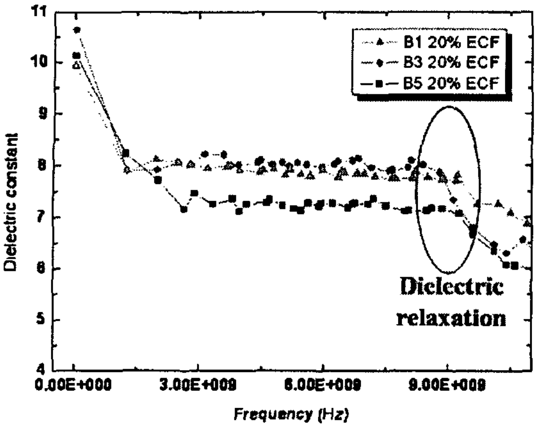


Fig. 9 Dielectric constant changes with frequency: BT powders 20vol% ECF

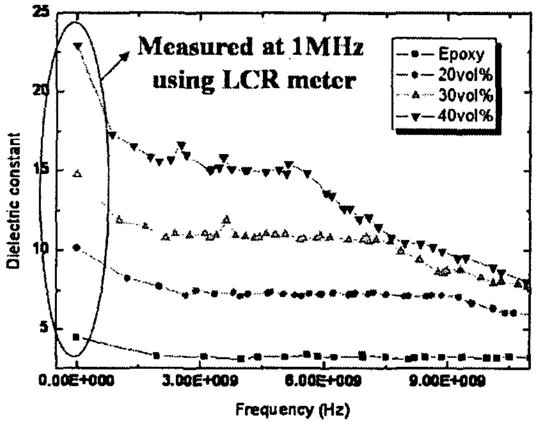


Fig. 10 Dielectric constant changes with frequency: B5 powder 0~40vol% ECF

Fig. 10 is shown dielectric constant changes of 0~40vol% ECFs with frequency about B5 powder. The dielectric constant of the B5 40vol% ECF at 1MHz is 23 but the dielectric constant over 0.5GHz measured using the cavity resonance method is about 17. This value at over 1GHz is approximately 3/4 of the value at 1MHz. This dielectric constant reduction is also observed in the case of the epoxy film. The dielectric constant of the epoxy is 4.3 at 1MHz but 3.2 over GHz, 3/4 of the value at 1 MHz. Effective dielectric constant of polymer/ceramic composite is proportional to the dielectric constant of polymer matrix. Therefore the dielectric constant reduction of ECF between 1 MHz~0.5GHz is due to the dielectric constant reduction of epoxy matrix. Above few GHz, dielectric constants abruptly decrease and dielectric relaxation occurs. These relaxation frequencies reveal at lower frequency as BT powder loading increases. It is due to increase of relative effect of $BaTiO_3$ powder with epoxy matrix.

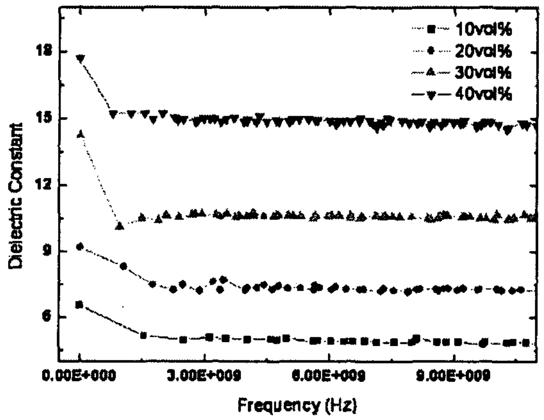


Fig. 11 Dielectric constant changes with frequency: S1 powder 10~40vol% ECF

Fig. 11 is shown dielectric constants of epoxy/$SrTiO_3$ composite with frequency. Up to 10GHz, there is no dielectric relaxation, and they only depended on the initial dielectric constant determined by the volume fraction of $SrTiO_3$ and on reduction of dielectric constant of polymer matrix. It is thought that epoxy/$SrTiO_3$ composites have same polarization mechanisms up to 10GHz about all the different loading of $SrTiO_3$ powders.

C. Embedded capacitor paste

Fig. 12 shows surface profiles of epoxy/$BaTiO_3$ composite layer deposited on PCB by screen-printing method after drying. Generally screen printing causes surface irregularity due to printing mask peel-off as shown in Fig. 12. After lamination using heat and pressure, surface uniformity was improved as sown in Fig. 12. Dielectric layer with more uniform thickness was obtained after the lamination. Fig. 13 shows cross-sectional SEM image of cured ECP layer on CCL after lamination.

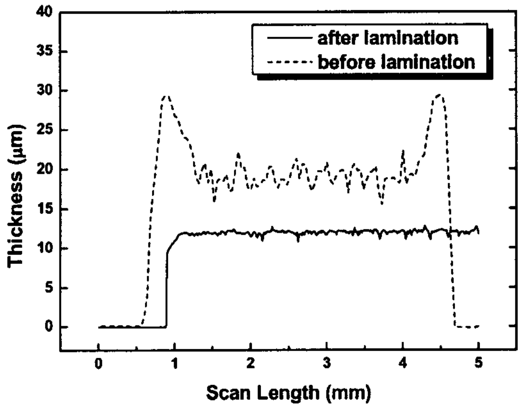


Fig. 12 Surface profiles before and after lamination.

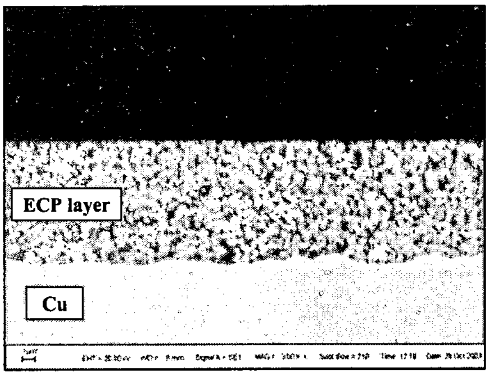


Fig. 13 SEM cross-section image of cured ECP layer on CCL after lamination

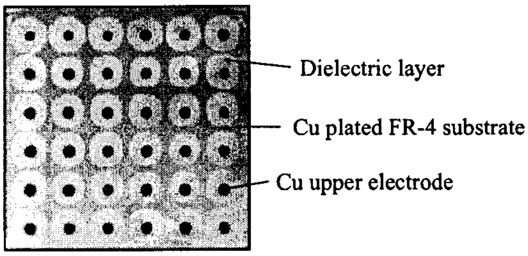
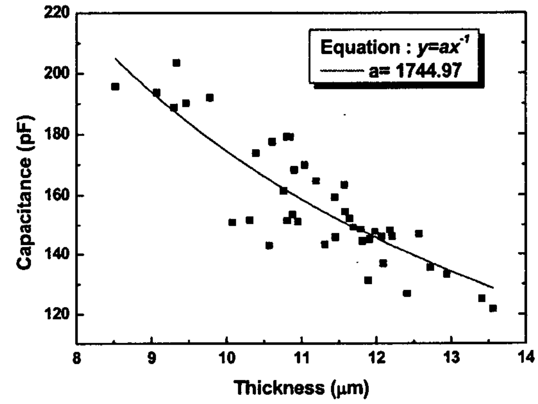


Fig. 14 Optical image of ECP capacitors fabricated on CCL

Fig. 14 shows optical image of ECP capacitors fabricated on a CCL using screen printing method. In order to measure dielectric constant more precisely, capacitors were formed on flat Al-deposited glass, and capacitance and thickness of each dots were measured. Fig. 15 shows capacitance change as a function of thickness. The measured results were fitted to the (3), where A is electrode area and d is dielectric layer thickness, and dielectric constant (ε_r) of ECP capacitors was estimated.

$$C = \varepsilon_0 \varepsilon_r \frac{A}{d} \tag{3}$$

Estimated dielectric constant of ECP dielectric layer was 63. This value is higher than the ECF containing same BT particle content. This is presumably due to densification by applying pressure during lamination. Average specific capacitance was 5.1nF/cm^2.



Fig, 15 Capacitance vs. dielectric layer thickness of ECP capacitors

CONCLUSION

Effects of BaTiO$_3$ powders on the dielectric constant of epoxy/BaTiO$_3$ composite embedded capacitor films were investigated using 5 different size BT powders and a ST powder. The highest dielectric constant was obtained from the 0.83㎛ size BT powder. The decrease of the dielectric constant below 0.83㎛ is due to the decrease of tetragonality, and the decrease of the dielectric constant above this size is presumably due to the reduction of 90° domain wall or surface area. About epoxy/ST composite ECF, dielectric constant is smaller than that of epoxy/BT composite, and there is no effect of particle size and tetragonality.

Dielectric constant of ECF in high frequency range (0.1~10GHz) was measured using cavity resonance method. By measuring resonance frequencies using network analyzer, dielectric constant of ECF was calculated. Calculated dielectric constants in this frequency range were about 3/4 of the dielectric constant at 1 MHz. This difference was due to the decrease of the dielectric constant of epoxy matrix. At 5~9GHz, dielectric relaxation of BT powder was observed, it was due to changing of polarization mode of BT powder. About ST powder, there was no relaxation up to 10GHz.

Capacitors fabrication using epoxy/$BaTiO_3$ composite embedded capacitor pastes was successfully demonstrated. In order to improve flatness of ECP dielectric layer, pressure was applied during curing. Thickness uniformity was significantly improved after lamination processes. Dielectric constant of the capacitor containing 50vol% BT powder was estimated to be about 63 at 100 kHz and 5.1 nF/cm^2 was achieved.

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