A Study on Epoxy/BaTiO3 Embedded Capacitor Pastes for Organic Substrates

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Abstract

In this work, embedded capacitor pastes (ECPs) with various BaTiO3 (BTO) powder contents were formulated and screen-printed on PCBs to fabricate capacitors. Material properties of ECPs such as rheology, curing behavior and dielectric constant were investigated. Using optimized ECPs, embedded capacitors were fabricated for reliability tests such as thermal cycling test and high temperature/humidity test.

ECP resin had curing process while temperature changed from 130°C to 220°C. All ECPs had sufficiently low viscosities at a shear rate of 100 sec-1 to be screen printed. The dielectric constant of cured ECP increased up to 60 at 70 vol%, and dielectric loss was about 0.023 for all ECPs regardless of BTO volume content. For the reliability test, ECPs with 50, 60, and 70 vol% BTO powder contents were selected, and embedded capacitors were fabricated. Thermal cycling test with a temperature range from -55°C to 125°C for 1000 cycles and high temperature/humidity test with 85°C/85RH% condition for 1000 hours were performed. After thermal cycling test, capacitance decreased about 5–10%, but dielectric loss was not changed. After 85°C/85RH% test, capacitance and dielectric loss increased about 20%. Capacitance changes after thermal cycling test was presumably due to high temperature exposure above T_g and water absorption to polymer matrix.

1. Introduction

Electronic systems are composed of active components such as ICs 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]. For example, the ratio of the passive to active components in mobile cellular phones is over 20 [2]. Currently most of the passive components are surface-mounted as discrete forms. Among passive components, capacitors have been most widely studied, because they can be used for various functions, such as decoupling, 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, into a form of embedded capacitors. Embedded decoupling capacitors can show better electrical performance due to reduced parasitic inductance.

Embedded capacitor materials are required to have high dielectric constant, low capacitance tolerance, good processability, and low cost. Up to now, however, any single material had not met these requirements. For example, thin film capacitor materials formed by a vacuum deposition have the advantage of fairly high capacitance, while they have drawbacks of high processing temperature and high cost.

Polymer/ceramic composite, polymer filled with ceramic powder is one of the most promising materials for embedded capacitors [3–5]. It has high dielectric constant of ceramic powders and good processability of polymers resulting in lower temperature process and lower cost. A spin coating method has been extensively used for depositing polymer/ceramic composites [5–7], because the spin coating method has the major advantage of thinner film fabrication resulting in higher capacitance. However, the spin coating method has major technical difficulties which should be solved. The first one is large waste of materials and the second one is non-uniform thickness control of films, which results in non-uniform electrical properties of capacitors over a large area. Recently, a tape casting method was suggested to fabricate polymer/ceramic composite films with uniform thickness [8]. Two methods previously mentioned have a limitation of not being able to form a capacitor layer in local area. It is not desirable because parasitic inductance occurs, if a dielectric layer is formed in the entire area on printed circuit boards (PCBs). Therefore, we designed screen-printable epoxy/BTO composite embedded capacitor pastes (ECPs). ECPs have the advantage of that capacitors can be formed locally in a desired part via mask pattern using a screen printing method. However, ECPs have a problem of high tolerance because the edge of a screen printed layer is generally thicker than its center due to surface tension of mask.

In this work, material formulation for ECPs was introduced. Material properties of epoxy/BTO composite embedded capacitor pastes (ECPs) such as curing behavior, viscosity, and dielectric constant were investigated as well. Embedded capacitors were fabricated for reliability tests such as thermal cycling test and high temperature/humidity test.

2. Experimental

2.1. Materials

2.1.1. ECP resin system

ECP basically consists of liquid Bisphenol-A type epoxy, thermoplastic polymer, solvent, BTO powder, and curing agent. Vinyl-type thermoplastic polymer with high molecular weight (~170,000) was used. Solvent was needed not only to dissolve solid thermoplastic polymer but also to reduce viscosity of ECP. This resin system has good screen-printability and good dimensional stability after screen-
printing. As a curing agent, dicyandiamide (DICY: \( \text{NH}_2\text{NHCNHCN} \)) was used. DICY is a latent curing agent for high temperature curing and curing reaction does not proceed at room temperature [9]. This enables handling to be easier because the viscosity of ECP does not change during fabrication process and screen printing process. In addition, screen-printed thick film layer can be kept in B-stage after drying process.

2.1.2. BTO powder

BTO has been widely known as a high dielectric constant material. Dielectric constant of bulk BTO is affected by its grain size at room temperature. Its dielectric constant increases up to a maximum with decreasing its grain size when its grain size is at approximately 0.9 µm, but decreases again with decreasing its grain size when its grain size is below 0.9 µm. The dielectric constant of bulk BTO is strongly dependent on the crystal structure of BTO. BTO powder has similar behavior to the dielectric constant of bulk BTO. At room temperature, tetragonality decreases as the particle size decreases slowly up to 0.3 µm. Tetragonality of BTO powder whose particle size is less than 0.3 µm rapidly decreases, and disappears when it became approximately 0.1 µm. It means the structure changes to cubic or pseudocubic structure [10-11]. Therefore, it can be expected BTO powder will have the maximum dielectric constant at approximately 0.9 µm and was also verified [8]. Therefore, BTO powder with average size of 0.9 µm was chosen. Fig. 1 shows a SEM image of BTO powder used in this study. However, the dielectric constant of BTO powder varies with fabrication methods. Moreover, its dielectric constant can be increased by post-treatment such as heat-treatment.

![Figure 1. SEM image of BTO powder.](image)

2.2. Fabrication process

2.2.1. Formation of ECPs

Fabrication processes of ECPs are as follows; 1) Liquid epoxy resin, thermoplastic resin, dispersant, and coupling agent were mixed in a rotational mixer for 3 minutes. 2) BTO powder was added to the mixture and mixed in a rotational mixer for 5 minutes. 3) To break agglomerates of BTO powder, the resin system had 3-roll mill mixing process 3 times. 4) After adding curing agent, the resin system had 3-roll mill mixing process one more time.

2.2.2. Curing and rheological characterization

Curing property of ECP resin was investigated using DSC (Differential Scanning Calorimetry). In dynamic scan mode, ECP resin was heated from 50ºC to 300ºC at a heating rate of 10ºC/min in nitrogen atmosphere. To measure cure times of ECP resin, isothermal scan was performed at various temperatures.

Rheological properties of ECPs were investigated using a plate-and-plate rotational rheometer. ECPs with various powder contents were sheared between a cone and a plate for 2 minutes as shear rates increased from 0 sec\(^{-1}\) to 100 sec\(^{-1}\). After shear rate came to a maximum value, shear rate decreased again from 100 sec\(^{-1}\) to 0 sec\(^{-1}\) for 2 minutes.

2.2.3. Capacitor fabrication and measurement

Using ECPs, metal-insulator-metal structures were fabricated. First, ECPs were printed on PCBs using DEK 248 screen printer. Conditions for screen printing are as follows; 1) Squeege hardness : 90 durometer, 2) Squeege angel : 45º, 3) Printing mask mesh : 250 mesh, 4) Mask emulsion thickness : 10µm, 5) Snap-off distance : 1mm , and 6) Printing speed : 30mm/s. Second, ECPs screen-printed on PCBs were dried on a hot-plate at 80ºC for 30 minutes to remove solvent. After the drying process, ECPs were cured in laminator at a pressure of 50 psi. Temperature profile for curing was 80ºC/30min and 180ºC/60min. The reason ECPs are kept at 80ºC for 30min is to give ECPs fluidity at B-stage. After the curing process, metal (Cu) top electrodes were deposited by a sputtering method using a shadow mask. The area of top electrode was 3.14 mm\(^2\). Fig. 2 shows a photo image of a fabricated capacitor sample.

The thickness of ECPs was measured using surface profiler (Alpha-step 500), and their capacitance and dielectric loss were measured at 100 kHz using HP 4284A LCR meter. Dielectric constant was calculated from the measured thickness and capacitance.

![Figure 2. Photo image of a fabricated capacitor sample.](image)

2.2.4. Embedded capacitor and reliability test.

To characterize material reliability of ECPs, embedded capacitors were fabricated. Fig. 3 shows a schematic diagram
of circuit designed for embedded capacitors and Fig. 4 shows fabrication process of embedded capacitors. First, ECPs were screen printed on patterned bottom electrodes. The area of screen printed ECP was larger than that of bottom electrode to use relatively flat part of the screen printed layer as an effective capacitor area. It is because the edge of screen printed layer is generally thicker than its center due to the surface tension of mask. Second, silver paste was screen printed on a cured ECP layer. As shown in Fig. 3, silver paste was connected to the other electrode to measure capacitance. The capacitance can be measured at the pads of backside of the sample. Finally, capacitors were embedded by pre-prag bonding process.

![Figure 3. Schematic diagram of circuit designed for embedded capacitor.](image)

For the reliability tests, three types of ECPs which contain 50, 60, and 70 vol% powder were selected as a capacitor material. Thermal cycling test (-55°C/15min ~ 125°C/15min) and high temperature/high humidity test (85°C/85RH%) were performed for 1000 cycles and 1000 hours, respectively. In addition, high temperature aging test was performed at 100 °C to investigate recovery of capacitance.

![Figure 4. Fabrication process for demonstration of embedded capacitor.](image)

### 3. Result and Discussion

#### 3-1. Curing property

Fig. 5 shows heat flow changes of ECP resin which contains no powder in dynamic scan mode. Fig. 6 shows degree of cure calculated from the Fig. 5 as a function of temperature. It can be found that curing of ECP resin starts at 130°C and ends at 220°C. Endothermic peak at about 230°C is a solvent vaporization peak. Fig. 7 shows heat flow changes of ECP resin at various temperatures. As shown in Fig. 7, exothermic reaction took place as scanning time increased and heat flow decreased again after curing. It is presumably due to the mass reduction by solvent vaporization. The end-point of curing is the maximum point of heat flow. X marks in Fig. 7 indicate the maximum points of heat flow. Cure times at various temperatures were summarized in Table 1. From the above results, drying condition and curing condition were set to 100 °C for 30 min and 180 °C for 60 min, respectively.

![Figure 5. Heat flow changes of ECP resin as a function of temperature.](image)

![Figure 6. Degree of cure of ECP resin as a function of temperature.](image)

![Figure 7. Heat flow changes of ECP resin at various temperature in isothermal mode.](image)
Table 1. Cure times of ECP resin at various temperature.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>180</th>
<th>200</th>
<th>220</th>
<th>240</th>
<th>260</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cure time (min)</td>
<td>41</td>
<td>32</td>
<td>22</td>
<td>5</td>
<td>3</td>
</tr>
</tbody>
</table>

3-2. Rheology

Fig. 8 shows viscosity curves of ECPs as a function of shear rate. Viscosities of ECPs gradually decreased as the powder contents increased within whole shear rate. ECPs had high viscosity at static state (~0 sec\(^{-1}\)) and low viscosity at high shear rate. All ECPs had low viscosity of about 100 cPs at a shear rate of 100 sec\(^{-1}\). It can be presumably understood that viscosity difference does not significantly affect surface roughness of the printed layer. Hysteresis area which means relative thixotropy increased as the powder contents increased. The increase of thixotropy with powder contents is due to the van der Waals force among particles. The particles form network structure at stand-by state and the network results in increase in viscosity. If shear force were applied to the pastes, the shear force would break down the network structure [12].

3-3. Dielectric constant

Fig. 9 shows thickness of cured layers as a function of powder contents. The thickness of an ECP layer increased as the powder contents increased. Although all ECPs were screen printed in same condition, the thickness of ECPs was different. The thickness difference is simply due to the amount of relative solvent content. ECPs with low BTO powder content have high volume portion of solvent. Therefore, ECPs with lower powder contents had thinner thickness than ECPs with higher powder contents after curing.

Fig. 10 shows specific capacitance of fabricated capacitors as a function of powder contents. The specific capacitance of ECP layers increases as the amount of powder increases. However, it reaches a maximum value at 60 vol%, and then decreases with further powder addition. This decrease in specific capacitance is due to the voids or pores remained in ECP layers to accommodate excess powders over the theoretical maximum packing density [13].

Based on the above results, dielectric constants of ECPs with powder contents were calculated. Fig. 11 shows dielectric constants of ECPs as a function of BTO powder contents. The dielectric constant of ECP increased up to about 60 as BTO powder content increased. As previously mentioned, the slow-down of dielectric constant increment above 60 vol% occurred because the powder packing density can not come to the theoretical maximum packing density. Considering solid content ratio, theoretical maximum packing
density is 72 vol%. However, it is too difficult to disperse powder uniformly at high volume powder content in an actual condition. Therefore, it can be thought that actual maximum packing density would be in the range from 60 to 70 vol% in single particle packing.

In thermal cycling test, dielectric losses were stable in whole cycles but relative capacitance rapidly decreased at initial stage and was stabilized around 0.9 after approximately 100 cycles. This is due to the relaxation of residual stress. It is widely known that residual stress of polymer matrix generated during curing process can be relaxed by exposure to high temperature above the glass transition temperature [14]. Polymer chains can freely move above glass transition temperature and total volume seems to macroscopically expand. Increase of free volume means the decrease of dielectric constant because the dielectric constant of free volume is 1. Therefore, overall dielectric constant of ECPs becomes lower [15].

3-4. Reliability test result

Fig. 12 shows photo images of an embedded capacitor. ECP layers and metal pads are shown through the semi-transparent FR-4 layer after pre-prag bonding. Fig. 13 shows thermal cycling test result of embedded capacitors. The capacitance of 50 vol% ECP was lower than that of 60 and 70 vol% ECP. On the other hand, the capacitances of 60 and 70 vol% ECP were almost same. It was similar to the specific capacitance result. As previously mentioned, decrease of capacitance is due to the voids or pores remained in ECP layers to accommodate excess powders over the theoretical maximum packing density.

Fig. 14 shows relative capacitance and dielectric loss changes during 85ºC/85RH% test and 100ºC aging test. In 85ºC/85RH% test, both dielectric loss and relative capacitance steadily increased. It can be understood that absorbed moisture changes molecular dipoles. Polar group of water increase polarity of ECPs, and it results in increase of
capacitance and dielectric loss [16-17]. Furthermore, the increasing rates of two parameters slowed down as the test time progressed. It was already reported that the slow down of increasing rate is presumably due to the saturation of moisture absorption [18-19].

In 100 °C aging after high humidity and temperature test, relative capacitance rapidly recovered within 200 hours. Relative capacitance stabilized around 0.9 after 200 hours. It was similar to the result of thermal cycling test and it is presumably understood that both moisture vaporization and polymer matrix relaxation occurred.

Conclusions

Screen-printable epoxy/BTO embedded capacitor pastes with high dielectric constant and good thermal stability were newly formulated. In terms of material formulation, ECPs are composed of high dielectric constant BTO powder, specially formulated epoxy resin, and latent curing agent. And in terms of fabrication process, a screen printing method was used to selectively fabricate dielectric layer in desired areas. The optimum curing condition of ECP resin was determined by the curing behavior results.

In case of ECP contain 70 vol% BTO powder, the dielectric constant increased up to about 60. The theoretical maximum packing density is 72 vol% but 60~70 vol% was desirable as actual packing density for processability. Actually, the increment in dielectric constant slowed down above 60 vol% because of because voids or pores entrapment in ECPs.

For the material reliability tests, embedded capacitor structure was demonstrated. Three ECPs which contain 50, 60, and 70 vol% powder were selected for the tests. In thermal cycling test, dielectric loss was stable, but relative capacitance rapidly decreased at an initial stage and then stabilized at 0.9 after approximately 100 cycles. It is understood that residual stress of polymer matrix generated during curing process can be relaxed by exposure to high temperature above glass transition temperature. In 85°C/85RH% test, both dielectric loss and relative capacitance steadily increased. It is understood that absorbed moisture affects molecular dipole change. In 100 °C aging after 85°C/85RH% test, relative capacitance and dielectric loss rapidly recovered within 200 hours. It is presumably understood that both moisture vaporization and polymer matrix relaxation occurred.

References