Study on the Epoxy/BaTiO₃ Embedded Capacitor Films Newly Developed for PWB Applications

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Abstract
Embedded passives technology is a promising method for miniaturization and higher electrical performance of electronic package systems. High dielectric constant epoxy/ceramic composites have been considered as embedded capacitor materials for organic substrates, because they have processability and compatibility with printed wiring boards (PWB), in addition to high dielectric constant.

In this work, we have developed embedded capacitor films with flexibility, processability, and uniform characteristics, and demonstrated epoxy/BaTiO₃ composite capacitor with small capacitance tolerance could be fabricated using the film. Curing temperature and amount of curing agent were optimized using differential scanning calorimeter (DSC) analysis. Dielectric constant of embedded capacitor films with BaTiO₃ powder volume loading was observed and this behavior is explained using SEM images and density measurement of the films.

As a result, using bimodal mixture of two different size BaTiO₃ powders, dielectric constant 100 was achieved. 7 µm thick capacitor film showed 10 nF/cm² with less than ± 5% tolerances, and low leakage current less than 10⁻⁸ A/cm² at 10 V was demonstrated.

1. Introduction
Electronic systems are composed of many electronic components such as semiconductors and passive components like resistors (R), inductors (L), and capacitors (C). The passive components become of increasing interest because the number of the passives is steadily growing as the electronics products are progressing toward higher functionality. [1] For example, the ratio of passive to active components in mobile cellular phone is over 20. [2] Currently these large number of passive components are surface-mounted as discrete format, so they do not only occupy large area of substrate but also lower electrical performance and reliability owing to long interconnection length and increase of the number of solder joint respectively. To solve these problems, embedded passive technology, which incorporates passive components into multi-layer substrates, has been actively investigated. Among the various embedded passives, embedded capacitors call for special attention as they are used in relatively large numbers for various functions such as signal de-coupling, switching noise suppression, filtering, and tuning.

Thin film capacitors formed by vacuum deposition have an advantage of fairly high capacitance, while at the same time they have drawbacks of high processing temperature and high cost. However, polymer/ceramic composites, which combine processing flexibility of polymer and high dielectric constant of ceramic, are promising materials as embedded capacitor dielectrics, because they use low-temperature and low-cost process and have compatibility with flexible organic boards. [3][4]

Most polymer/ceramic capacitor films have been fabricated from solution spin coating which has a major advantage of thinner films, and hence, higher capacitance. However, the major technical challenges faced in spin coating are two fold; first, there is a large waste of materials and second, film thickness control over large area is not easy, which, in hence, results in non-uniform electrical properties of capacitors over large area.

In this paper, we fabricated embedded capacitor film for PWB applications and demonstrated that epoxy/BaTiO₃ composite capacitor with excellent properties could be successfully fabricated using the film format. Characteristics of the embedded capacitor film are flexibility, good film formation capability, long shelf life, stability at high temperature, and uniform thickness and dielectric constant over large area. Film formulation, optimum amount of curing agent, powder volume loading effects, and some characteristics of the capacitors fabricated using the embedded capacitor films will be discussed.

2. Experimental Procedures
a. Materials
BaTiO₃ was chosen as ceramic particles because it is a well-known and widely-used high dielectric constant powder. The dielectric constant of BaTiO₃ powder varies as a function of particle size; it reaches its maximum value around the particle size of 1µm, decreasing as the particle size becomes smaller than 1µm. [5] This is explained by the tetragonality of the BaTiO₃ particles, which reduces as the particle size decreases. [6] Hence particle size is a very important factor in selection of BaTiO₃ powders to fabricate a high dielectric constant composite film. In addition to the particle size, how to maximize packing of those BaTiO₃ particles is critical to get higher dielectric constant of capacitor film. It is known that the theoretical maximum packing density from spherical particles of single size is approximately 74vol%. However, the packing density can be further increased by introducing a bimodal distribution of BaTiO₃ particles in which finer particles can fill in interstitial sites between coarser particles. The higher the ratio of the size of coarser particles to that of finer particles, the better the packing density we can obtain. [7] In this work, to meet the two facts above mentioned, two kinds of BaTiO₃ powders were used; powder-A is 0.9µm and powder-B is 0.06µm in diameter. Size and shape of the powders can be seen in figure 1. From X-ray diffraction patterns shown in figure 2, we can conclude that the powder-A has tetragonal structure and the powder-B has cubic structure. Based on these results, we can expect that capacitor
films made of BaTiO$_3$ powder-A would show higher dielectric constant than those made of BaTiO$_3$ powder-B.

Fig. 1. SEM images of (a) Powder A (0.9 µm) and (b) Powder B (0.6 µm)

Phosphate ester was used as a dispersant and 2-Butanone (MEK) and Toluene mixture was used as a solvent. [8]

Specially formulated epoxy resin was used as a polymer matrix. The resin is composed of thermoset epoxy and thermoplastic phenoxy. This resin combination was originally designed for anisotropic conductive adhesive films (ACAF), for purpose of good flexibility and tackiness of uncured film, and good adhesion strength and high temperature stability after curing. [9] DICY, a latent curing agent, was selected as hardener for long shelf life. [10]

**b. Dispersant optimization**

The suspension made of BaTiO$_3$ particles, dispersant, and solvent was ball-milled for 48 hours, and then a viscosity test was conducted according to the amount of dispersant to decide the optimum amount of dispersant. The amount of dispersant set for particle A (0.9 µm in dia.) was 1.0, 1.2, 1.4, 1.6wt% while for particle B (0.06 µm in dia.) it was set to 2.5, 3, 4, 5, 8wt%. In both cases, the particle volume loading was set to 33.3vol%.

**c. Film formation**

The epoxy resin dissolved in MEK/Toluene solution, and the suspension containing BaTiO$_3$ powders, dispersant, and curing agent, was mixed. Then the mixed solution was poured on releasing film and doctor-bladed using a automatic film coater. (in figure 3) And drying the film was performed at 80°C for 3 min in a convection oven.

**d. Curing agent optimization**

To optimize the amount of curing agents and curing temperatures, capacitor films with the curing agent amount of 2, 5, 10, 14, 16, 18, 20wt% were fabricated. DSC (differential scanning calorimeter) thermal analysis of the films was conducted, and the enthalpy energy change from 25°C to 250°C was observed. In this experiment, the BaTiO$_3$ particle condition was set to a volume loading of 65vol% of particle A. The figure 4 shows the process of capacitor films formation and capacitors fabrication.

**e. Capacitor fabrication and characterization**

Capacitor films were laminated on Si wafers sputtered with 0.5µm thickness of aluminum for bottom electrode. The pre-lamination was at 110°C with 55psi pressure for an hour for pre-adhesion and evaporation of remaining solvents. And then final lamination was kept at 200°C for 30 min for full curing. After lamination, 0.5 µm thick aluminum cap
electrodes were deposited on capacitor films by sputtering. The shadow mask was employed to form top electrodes of 0.126 cm² area.

The thickness of capacitor films was measured by an alpha-step. Film density was calculated using Archimedes principle. Capacitance and dielectric loss were measured using a HP 4284A LCR meter at a frequency of 100kHz. Leakage current was measured by a Keithley 236 Source Measure Unit with the bias up to 5MV/m.

The viscosity behavior of two BaTiO₃ particles suspensions is shown in figure 5. Pseudoplastic behavior was observed in both cases. The amounts of optimum dispersant at the minimum viscosity were observed at 1.4wt% for powder-A, and 4.0wt% for powder-B. The apparent viscosity of the suspension containing powder-A was higher than that containing powder-B, due to stronger Wan der Valls forces of the smaller powder.

B. Curing behavior with the amount of DICY

Figure 6(a) shows the behavior of enthalpy energy changes as a function of temperature. The data was plotted as dΔQ/dt vs. temperature, which is related to heat capacity. The positive value of dΔQ/dt represents an endothermic reaction, while negative value represents an exothermic reaction. Curing causes an endothermic shift in the initial baseline because of the increased heat capacity due to polymerization. Hence, it was observed from figure 6(a) that epoxy resin curing by DICY began at temperature greater than 160°C. This temperature is actually a bit higher than the known curing temperature of DICY, 140–160°C. This difference was considered to originate from the interruption of curing of polymer by BaTiO₃ particles dispersed in the resin. For curing agent less than 14wt%, the endothermic peaks were broad. The peaks tended to be sharpened for curing agents larger than 14wt%, and the curing peak temperature was 180°C.

Fig. 5. Viscosity changes as a function of the amount of dispersant for (a) Powder A, (b) Powder B

The peak areas, which are directly related to enthalpy energy changes in the sample, were plotted against temperature shown in figure 6(b). It could be observed from figure 6(b) that the reaction enthalpy energy reached its maximum value at 14wt%, and gradually decreased for the amount of curing agent larger than 14wt%.

Therefore taking into consideration of shapes of the peak and the amount of enthalpy energy of curing, optimum amount of curing agent was determined at 14wt% of the resin.
Fig. 6. Differential scanning calorimeter analysis; (a) DSC traces of capacitor films and (b) endothermic energy as a function of the amount of curing agent.

C. Powder volume loading effects

Figure 7 shows dielectric constant of capacitor films as a function of total powder volume loading. In this figure, unimodal means the use of only one powder, the powder-A, and bimodal means the use of the powder-A and the powder-B mixture (mixing ratio was 4:1). In unimodal case, the maximum dielectric constant of 65 was obtained at 73 vol%. However there was a sudden drop of dielectric constant past the 73 vol%. In bimodal case, maximum dielectric constant of 90 showed up at higher volume loading, 80 vol% and also there was a sudden drop past the 80vol%. Using bimodal mixture, 40% improvement of maximum dielectric constant was achieved compared with the value of unimodal case. This improvement is presumably due to the increase of packing density and this will be discussed later.

Fig. 7. Dielectric constant as a function of powder volume loading

Figure 8 (a) and (b) show the SEM images of film morphology of unimodal and bimodal, respectively. White spots are BaTiO$_3$ particles and black background is polymer resin or void. In case of the unimodal distribution, as the BaTiO$_3$ particle content increased, it was found that the

(a) Unimodal

(b) Bimodal

Fig. 8. Film surface morphology with increasing particle volume loading in (a) unimodal and (b) bimodal.
packing grew denser up to particle loading of 73 vol%. At 80 vol%, however, more voids than at 73 vol% was clearly observed at 80 vol%. In case of the bimodal, particles seemed to be more closely packed than those of unimodal film in same amount of powder loading, and the packing became denser up to 80 vol% powder loading, where the optimal packing density occurs, and then decreases at 85 vol% as shown in the unimodal.

Figure 9 shows the variation of calculated (from material formulation) density and measured (by Archimedes’ principle) density of the films with increasing particle volume loading for both unimodal and bimodal distribution. On the whole density of bimodal distribution was higher than that of unimodal distribution, but lower than that of the calculated. This difference between the calculated values and the measured values is presumably due to defects or voids occurring during drying and curing process. It could be observed that the density graphs for both the unimodal and the bimodal were very similar to the graph of dielectric constant versus particle volume loading. The maximum film density was obtained at 73 vol% for unimodal and 80 vol% for bimodal distribution, which are the points where the maximum dielectric constant was obtained. Therefore it is concluded that the decrease of dielectric constant at 80 vol% in unimodal film and at 85 vol% in bimodal film, in spite of the increase of high dielectric constant particles content, was caused by decrease of film density due to defects or voids originated from the disruption of closed packing arrangement by excess powders and solvent vaporization.

Figure 10 is a graph showing leakage current at the bias of 1 MV/m as a function of the particle volume loading in bimodal distribution. Below 60 vol%, small increase in leakage current with powder volume was observed. However, there was abrupt increase over 70 vol%. This can be explained using percolation phenomena. BaTiO3 powder is more conductive than polymer resin. At low volume loading of powder less than 70 vol%, the particles exist separately if they are well dispersed, and polymer resin blocks leakage current flowing. However as particle loading goes up, films become crowded by BaTiO3 particles and the particles start touching each other, that is, percolation occurs. So through the conduction path formed by the contacting particles current can flow more easily.

Table 1. Summary of the properties of the epoxy/BaTiO3 capacitor films with increasing powder loading in bimodal

<table>
<thead>
<tr>
<th>Particle volume loading (vol %)</th>
<th>20</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>73</th>
<th>80</th>
<th>85</th>
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<tr>
<td>Thickness (µm)</td>
<td>47.75</td>
<td>21.51</td>
<td>13.17</td>
<td>48.55</td>
<td>40.79</td>
<td>43.34</td>
<td>37.89</td>
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<tr>
<td>Dielectric constant</td>
<td>9.99</td>
<td>10.27</td>
<td>20.61</td>
<td>29.00</td>
<td>47.07</td>
<td>89.32</td>
<td>84.64</td>
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<tr>
<td>Dielectric loss</td>
<td>0.0276</td>
<td>0.0244</td>
<td>0.0238</td>
<td>0.0222</td>
<td>0.0200</td>
<td>0.0268</td>
<td>0.0386</td>
</tr>
<tr>
<td>Specific capacitance (nF/cm²)</td>
<td>0.19±0.01</td>
<td>0.42±0.02</td>
<td>1.39±0.06</td>
<td>0.53±0.03</td>
<td>1.02±0.05</td>
<td>1.82±0.09</td>
<td>1.98±0.09</td>
</tr>
<tr>
<td>Capacitance tolerance (± %)</td>
<td>5.3</td>
<td>4.8</td>
<td>4.3</td>
<td>5.7</td>
<td>4.9</td>
<td>4.9</td>
<td>4.5</td>
</tr>
<tr>
<td>Leakage current (nA/cm²) at 1MV/m</td>
<td>0.29</td>
<td>0.20</td>
<td>0.77</td>
<td>0.77</td>
<td>3.19</td>
<td>50.26</td>
<td>303.12</td>
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Table 2. Some properties of another epoxy/BaTiO₃ composite capacitors made from the ECF

<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th>Unimodal – powder A</th>
<th>Unimodal – powder B</th>
<th>Bimodal</th>
</tr>
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<tr>
<td></td>
<td>6.04</td>
<td>15.1</td>
<td>11.74</td>
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<tr>
<td>Dielectric constant</td>
<td>70</td>
<td>44</td>
<td>102</td>
</tr>
<tr>
<td>Dielectric loss</td>
<td>0.029</td>
<td>0.026</td>
<td>0.029</td>
</tr>
<tr>
<td>Specific capacitance (nF/cm²)</td>
<td>10.25 ± 0.18</td>
<td>2.59 ± 0.16</td>
<td>7.70 ± 0.32</td>
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<tr>
<td>Capacitance tolerance (± %)</td>
<td>1.75</td>
<td>6.17</td>
<td>4.15</td>
</tr>
<tr>
<td>Leakage current (A/cm²) at 10V</td>
<td>9.04 × 10⁻⁸</td>
<td>1.91 × 10⁻⁸</td>
<td>5.08 × 10⁻⁸</td>
</tr>
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</table>

5. Acknowledgements
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References