Relationships Between Suspension Formulations and the Properties of BaTiO$_3$/Epoxy Composite Films for Integral Capacitors

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Abstract
Although integral capacitors fabricated using polymer/ceramic composite film have been intensively investigated, there was no systematic study of relationships between suspension formulation and properties of capacitors made from the suspension. In this paper the effects of the suspension formulation such as powder size, amount of dispersant, and amount of solvent, on the capacitor properties such as dielectric constant, dielectric loss, leakage current were investigated using BaTiO$_3$ as a ceramic filler and epoxy resin as a polymer. It was found that high packing density could not only provide high dielectric constant and high capacitance but also high leakage current.

Introduction
Electronic circuit is composed of active components such as ICs and many passive components such as resistors, capacitors, and inductors. The number of the passive components is much bigger than that of the passive component [1]. These passive components are currently surface-mounted on a substrate in discrete type so that they occupy large area and result in parasitic loss due to long interconnection length. Especially as frequency used goes up, these problems become more serious. So it is thought that passive components will become a barrier to achieve miniaturization and high performance of electronic products. To solve these problems integral passive technology which incorporates passive components into multi-layer substrate is being actively investigated.

Among the integral passives, integral capacitor is receiving much attention because of its large demands and importance in electronic circuit [1]. The integral capacitors developed until now can be classified into two kinds by deposition method of dielectric materials; one is thin film capacitor using vacuum deposition such as CVD, sputtering [2], etc., and the other is polymer/ceramic composite capacitor [3,4]. Generally thin film capacitors have good electrical properties, but process temperature and fabrication cost are very high. In contrast the polymer/ceramic composite capacitor is to combines high dielectric constant of ceramics and processing flexibility of polymers [1]. They use easy, low cost process and have compatibility with printed wiring boards (PWBs).

To make polymer/ceramic composite capacitors, ceramic suspension containing ceramic particles, epoxy resin, solvent and other organics should be used. Capacitor properties are directly affected by how to prepare the suspension. Therefore correlations between suspension formulation and the properties of capacitors fabricated from it are very important.

If we know these correlations, we can control capacitor properties and get capacitors having characteristics we want. But until now interest of most of researches was focused on high dielectric constant of composite films and there was no systematic study to these relationships.

This work is a preliminary study to examine relationships between suspension formulation and properties of capacitors made from it. Using BaTiO$_3$ as ceramic particle and epoxy as polymer, we want to know how the capacitor properties such as dielectric constant, dielectric loss, and leakage current, are affected by powder size, amount of dispersants, and amount of solvent.

Experimental
a. Materials
Suspension was composed of BaTiO$_3$ powder, dispersant, solvent and epoxy. We used four different BaTiO$_3$ powders and details about them are shown in Table 1. As a dispersant phosphate ester (BYK-W 9010, BYK Chemie), well known dispersant for the dispersion of BaTiO$_3$ particles [5], was used. Propylene glycol methyl ether acetate (PGMEA; Aldrich) was used as a solvent, dispersing medium. Epoxy used in this study was Probelc LMB 7081 (Ciba-Geigy), photo-definable epoxy.

Table 1. Details of the Powders Used in this study

<table>
<thead>
<tr>
<th>Powders</th>
<th>Manufacturer</th>
<th>Diameter (µm)</th>
<th>Density (g/cc)</th>
<th>Specific surface area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BT-Ferro</td>
<td>Ferro Corp.</td>
<td>1.05</td>
<td>5.5</td>
<td>3.2</td>
</tr>
<tr>
<td>BT-T</td>
<td>TPL Inc.</td>
<td>0.05</td>
<td>5.7</td>
<td>14.51</td>
</tr>
<tr>
<td>BT-8</td>
<td>Cabot Corp.</td>
<td>0.2</td>
<td>5.9</td>
<td>8.5</td>
</tr>
<tr>
<td>BT-16</td>
<td>Cabot Corp.</td>
<td>0.06</td>
<td>5.9</td>
<td>16.8</td>
</tr>
</tbody>
</table>

b. Suspension Formulation and Capacitors Fabrication
After the dispersant was dissolved into the solvent, the powders were dispersed into that solution and ball mill was performed for 1 day. Then the epoxy was added to this slurry and ball mill was performed for 1 day once again. Quantities about powder, dispersant, solvent and epoxy will be mentioned for each experiment later.

With this suspension, MIM capacitors were fabricated on Si-wafer. The suspension were spin-coated (4000 rpm-30sec) on the Si-wafers on which aluminum blanket (0.5µ-) for bottom electrode had been deposited. After drying in the condition of 90°C and 15 min, ultraviolet (UV) light was applied to the films and the films were cured in the condition of 165°C and 1 hour. Using shadow mask aluminum top
electrodes of circle shape (thickness: 0.5μ-, area: 0.1257cm$^2$) were deposited by sputtering.

**c. Characterization**

Crystal structure of each powder was analyzed by X-ray diffraction (Cu Kα). Viscosity of the slurry containing solvent, powder, and dispersant was measured using Brookfield viscometer (LVDV-Ψ±). Thickness of the films was measured with Alpha-step.

Capacitance, dielectric loss, and leakage current were measured to characterize the capacitors. Capacitance and dielectric loss was measured with HP 4193 Impedance analyzer at 100 kHz. Leakage current was measured with Kethley 236 Source Measure Unit. Applying bias from 0 to 0.1 MV/cm according to the thickness of each film, the value at 0.1 MV/cm was checked.

**Results and Discussions**

(1) **Crystal structures of the powders**

Crystal structure of BaTiO$_3$ is cubic above 120°C, tetragonal in room temperature, orthorhombic below 10°C. BaTiO$_3$ shows paraelectric properties in cubic structure but ferroelectric properties in tetragonal structure. High dielectric constant and ferroelectric properties of BaTiO$_3$ comes from the tetragonal structure. Dielectric constant of BaTiO$_3$ strongly depends on particle size. According to some reports when grain size is approximately 1μ-, dielectric constant shows maximum around 5000~6000 and decreases drastically as grain size reduces [6]. The origin of the decrease of dielectric constant is attributed to the reduction of tetragonality with the decrease of particle size [7].

Looking over XRD patterns of the four powders (Fig. 1), we can see peak-split around 45° in the case of the BT-Ferro, but not clearly in the case of the other powders. Consequently it is thought that tetragonality of the BT-Ferro is high compared to the other powders. This agrees well to the fact that the size of BT-Ferro was the biggest (1.05μ-).

![Figure 1. XRD patterns of four different powders](image)

It is very hard to determine crystal structure from XRD pattern of BaTiO$_3$, because peaks of both phases show up at nearly similar positions and the only difference in the XRD pattern between tetragonal and cubic phase is peak-split occurring in tetragonal phase. In the case of tetragonal structure, peak-splits occur around 45°, 51°, 56°, and 66°. Among these, peak-split around 45° is relatively clearly discernable because intensity of two peaks is adequate and the gap between the two peaks is large compared to other peaks [8].

![Figure 2. Apparent viscosity of (a) BT-TPL, (b) BT-8, (c) BT-16, and (d) BT-Ferro](image)
(2) Viscosity Measurements

Fig. 2(a), 2(b), and 2(c) shows the rheological behaviors of three \( \text{BaTiO}_3 \) (BT-TPL, BT-8, and BT-16 respectively) suspensions (powder:solvent = 1:2) as a function of amount of phosphate ester. (Unit of the amount of phosphate ester is weight % of amount of the powder used) It was reported that electrostatic repulsive force plays a significant role in the dispersion of \( \text{BaTiO}_3 \) in organic media [9]. All suspensions showed shear thinning behavior, that is, viscosity decreased as shear rate increased. Minimum of apparent viscosity of each suspension containing BT-TPL, BT-8, and BT-16 occurred at dispersant of 4 wt%, 2 wt%, and 4 wt% respectively. Increase of the viscosity above the minimum dispersant value is possibly due to the reduction of electric double layer thickness resulted from increase of ion concentration resulted from the dispersant.

Fig. 2(d) shows the rheological behaviors of BT-Ferro suspension (containing the powder of 4cc) as a function of amount of solvent (5~8cc). Amount of dispersant was 1 wt% of BT-Ferro powder. It was natural that the more solvent, the lower viscosity was measured.

(3) Capacitor Chraterizations

a. Effects of dispersant

Fig. 3 shows electrical properties of the capacitors fabricated using the BT-TPL powder as a function of dispersant amount ( The ratio of epoxy to the powder was 1:3 ⇒75 vol%).

b. Effects of solvent quantity

Fig. 4 shows the capacitance and leakage current of the capacitors (80 vol% solid loading) fabricated using BT-Ferro powder as a function of solvent quantity. Amount of dispersant was 1 wt% (of the powder) for each samples.

Capacitance increased as the addition of the solvent increased. The increase of capacitance resulted from the fact that as solvent increased, the viscosity of suspension reduced as shown in Fig. 3(d) and the thickness of the resulted film decreased. Dielectric constants of the four samples were around 55 but dependence on solvent quantity was not found. Dielectric loss of the films was about 0.02 and also the dependence on the solvent quantity was not found.

Figure 3. Dielectric and Electrical Properties of the capacitors using BT-TPL

Figure 4. Capacitance and Leakage Current of the Capacitors Fabricated Using BT-Ferro

However leakage current increased with the increase of the solvent amount. Origin of this increase of leakage current cannot be explained thoroughly now, but one way to explain this could be related to better packing of particles resulted from reduced viscosity when we use more solvent. Surface of the particles coated with phosphate ester may be relatively conductive because the phosphate ester is an ionic dispersant. If the viscosity of a suspension is so low that the particles coated from the suspension can pack closely and homogeneously, contact between the particles will occur and network of the particles will form. Current can flow along this network, that is, along the conductive surface of particles.

Anyway it was demonstrated that the increase of solvent quantity did not only give positive effect of the increase of capacitance, but also give negative effects of the increase of leakage current.

c. Properties of Capacitors with BT-8 and BT-16

Properties of the capacitors fabricated using BT-8 and BT-16 were summarized into Table 2. Ratio of solvent to powder ratio was 2:1 and amount of dispersant was 2 wt% for BT-8
and 4 wt% for BT-16. These values are the ones determined through viscosity measurement shown in Fig. 2(b) and 2(c).

Dielectric constant of both capacitors calculated from capacitance was about 50. This value was a little lower than that of the BT-Ferro capacitors. As it can be seen from Fig. 1, it is thought that this difference came from the difference of tetragonality of the powders. In the case of BT-TPL, even lower value (30) was obtained. Since solid content in composite films with BT-TPL was less than those of other samples, it cannot be compared to others directly. But we can say that the much lower dielectric constant of the BT-TPL might be related to particle size. Consequently too small powder should be avoided to make high dielectric constant composite films.

| Table 2. Properties of the capacitors with BT-8, BT-16, and Ferro+8 |
|-----------------|-----------------|-----------------|
| Powder          | BT-8            | BT-16           | Ferro+8         |
| Solid volume loading | 80 vol%      | 80 vol%        | 80 vol%        |
| Capacitance (nF/cm²) | 23.79         | 18.04          | 46.3           |
| Dielectric loss  | 0.0236          | 0.0308         | 0.0233         |
| Dielectric constant | 50             | 50             | 93             |
| Leakage current (A/cm²) | 3.05×10⁻⁷    | 9.17×10⁻⁷     | 6.26×10⁻⁴     |

d. Effects of BT-Ferro and BT-8 powder mixing

Capacitors were made with mixing BT-Ferro and BT-8; the ratio of the BT-Ferro to the BT-8 was 3:1. Properties of the capacitors (80 vol% solid loading) were summarized in Table 2.

Capacitance was 46.3 nF/cm² and this corresponded to dielectric constant of 93. This high dielectric constant is due to high packing density as shown in Fig. 5. It is well known that packing density can be increased by introducing a bimodal distribution of particles in which finer particles can fill in the interstitial sites between coarser particles [10]. We can see a lot of voids when we use only single powder (BT-Ferro) as shown in Fig. 5(a). But the voids were filled up with the smaller particles by using the mixture of BT-8 and BT-Ferro as shown in Fig. 5(b). It is expected that higher dielectric constant can be obtained if we optimize the ratio of two powders.

By the way, in spite of this high dielectric constant there was a serious problem, too high leakage current. The leakage current was 6.26×10⁻⁴ A/cm² at 0.1 MV/cm, the highest value in this experiment. As mentioned earlier, this could result from the high packing density and the conduction path formation by the contact between particles.

Conclusions

Effects of suspension formulation on properties of the BaTiO₃/epoxy composite capacitors were investigated. Dispersant (phosphate ester) is necessary to improve dipersion of BaTiO₃ particles in organic medium but too much concentration give harmful effect, that is, the increase of dielectric loss and leakage current, because the phosphate easter remaining in the composite film can act as an impurity. Increase of solvent in suspension reduced viscosity of the suspension and made film thickness smaller, so that capacitance increased. But leakage current also increased. Using bimodal distribution extremely high dielectric constant (93) was obtained. But this method also caused large increase of leakage current. In conclusion, higher packing density can provide higher dielectric constant, but also higher leakage current, so that when we say dielectric constant leakage current also should mentioned together.

Figure 5. SEM Images of (a) BT-Ferro/Epoxy Composite Film surface (×100,000) and (b) Ferro+8/Epoxy Composite Film surface (×20,000)

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